AD-A039 805 HONEYWELL INC MINNEAPOLIS MINN SYSTEMS AND RESEARCH --ETC F/G 11/3
EROSION RESISTANT AR COATINGS FOR IR WINDOWS.(U)
FEB 77 W W DOERFFLER, H Y MAR, T BOORD F33615-76-C-5039

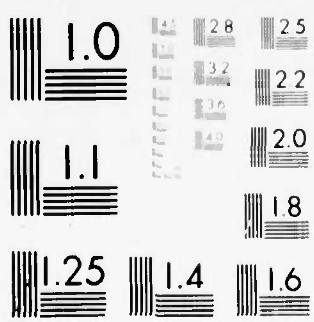
UNCLASSIFIED 77SRC15 AFML-TR-77-8 NL

1 OF 1
AD
A039805

END

DATE
FILMED
6-77

0398



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963-A

AFML-TR-77-8

18

12

EROSION RESISTANT AR COATINGS FOR IR WINDOWS

HONEYWELL, INC.
SYSTEMS AND RESEARCH CENTER
2600 RIDGWAY PARKWAY
MINNEAPOLIS, MN 55413

FEBRUARY 1977

TECHNICAL REPORT AFML-TR-77-8
FINAL REPORT FOR PERIOD DECEMBER 1976 - FEBRUARY 1977

AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or coporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

David W. Fischer
Project Monitor

William G. D. Frederick
Chief
Laser & Optical Materials Branch
Electromagnetic Materials Division
Air Force Materials Laboratory

Copies of this report should not be returned unless return is required by security consideration, contractual obligations, or notice on a specific document.

AIR FORCE - 3 MAY 77 - 100

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (WHEN DATA ENTERED)

19 REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER (18) AFML-TR-77-8	2. GOV'T ACCESSION NUMBER	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (AND SUBTITLE) (6) EROSION RESISTANT AR COATINGS FOR IR WINDOWS.		5. TYPE OF REPORT/PERIOD COVERED (9) Final Rep[redacted]t. Dec[redacted]76-Feb[redacted]77
		6. PERFORMING ORG. REPORT NUMBER (14) 77SRC15
7. AUTHOR(S) (10) W. W. Doerffler, H. Y. B. Mar, T. Boord, J. Brown		8. CONTRACT OR GRANT NUMBER(S) (15) F33615-76-C-5039 (17) 04
9. PERFORMING ORGANIZATIONS NAME/ADDRESS Honeywell, Inc., Systems & Research Center 2600 Ridgway Parkway Minneapolis, MN 55413		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS (16) Project No. 2303 Work Unit No. 2303Q405
11. CONTROLLING OFFICE NAME/ADDRESS Air Force Materials Laboratory (LPO) Air Force Systems Command Wright-Patterson AFB, Ohio 45433		12. REPORT DATE (11) 23 Feb[redacted]77
		13. NUMBER OF PAGES 65
14. MONITORING AGENCY NAME/ADDRESS (IF DIFFERENT FROM CONT. OFF.) (12) 65 p.		15. SECURITY CLASSIFICATION (OF THIS REPORT) Unclassified
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (OF THIS REPORT)

Unlimited distribution.

61102F

17. DISTRIBUTION STATEMENT (OF THE ABSTRACT ENTERED IN BLOCK 20, IF DIFFERENT FROM REPORT)

Unlimited distribution.

18. SUPPLEMENTARY NOTES

19. KEY WORDS (CONTINUE ON REVERSE SIDE IF NECESSARY AND IDENTIFY BY BLOCK NUMBER)

Antireflection coatings
Rain erosion resistant coatings
NdF_3, LaF_3, ThF_4, ZnSe coatings
Two layer AR coatings
ZnS, GaAs IR windows

20. ABSTRACT (CONTINUE ON REVERSE SIDE IF NECESSARY AND IDENTIFY BY BLOCK NUMBER)

Feasibility of rain erosion resistance of two layer AR coatings on ZnS small sample windows with good surface finish has been demonstrated. When exposed to 1 inch/hour simulated rainfalls for 20 minutes at a relative drop impact velocity of 470 mph, transmission losses of about 10 percent occurred.

HD-168 REV 11/74

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (WHEN DATA ENTERED)

402 349

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (WHEN DATA ENTERED)

The same coating combinations ($ZnSe/NdF_3$, $ZnSe/LaF_3$ and $ZnSe/ThF_4$) exhibited severe degradation after rain erosion testing when prepared on GaAs windows. The surface finish of the substrate windows appears to be an important factor for rain erosion resistance of coatings. ZnS and GaAs which did not meet the scratch and dig requirement of 60/40 exhibited poor rain erosion resistance of coatings. ZnS windows which exceeded the 60/40 requirement (close to 40/20) exhibited superior rain erosion resistance of deposited coatings.

SECURITY CLASSIFICATION OF THIS PAGE (WHEN DATA ENTERED)

PREFACE

This is the final technical report to the Air Force Materials Laboratory for the project to develop erosion resistant AR coatings for IR windows. This work was performed under Air Force Contract No. F33615-76-C-5039. Mr. D. W. Fischer, AFML/LPO, was the project monitor. Mr. T. L. Peterson, AFML/MBE, conducted the rain erosion testing.

This project was performed at Honeywell Inc., Systems and Research Center, 2600 Ridgway Parkway, Minneapolis, MN 55413. Dr. W. W. Doerffler was the principal investigator. The coatings design and computer analysis was performed by Dr. W. T. Boord and Mr. R. K. Daggit. Mr. J. L. Brown was responsible for the coatings preparation and testing. The MTF measurements and related analysis were performed by Mr. R. E. Zirkle, Mr. E. Bernal (Honeywell Corporate Research Center) and Mr. A. J. Mundy.

Routine MTF measurements were performed at Honeywell's Radiation Center (Lexington, MA).

TABLE OF CONTENTS

TABLE OF CONTENTS (concluded)

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (concluded)

LIST OF TABLES

SECTION I

INTRODUCTION AND SUMMARY

IR window materials for apertures on multi-sensor systems of high performance aircraft must possess the following properties:

- High transmittance over the wavelength range of interest
- Rain erosion resistance
- High-temperature (200°C) stability
- Low-cost for sizes up to 12" x 18" x 3/4"

ZnS and GaAs are candidate IR window materials for certain limited applications. IR windows, as received, exhibit reduced optical transmission in the visible and infrared wavelength regions due to bulk optical absorption and high surface reflection.

Antireflective (AR) coatings are required to reduce the surface reflection and thus inversely increase transmission. Specifically, the program goals for transmission were as follows: $\geq$ 60 percent between 0.5 μm and 0.9 μm and at 1.06 μm; and $\geq$ 95 percent between 8 μm and 10.5 μm for coated ZnS windows; and $\geq$ 95 percent between 8 μm and 12 μm for coated GaAs windows. Since the coated window is exposed to aerodynamic heating (up to 200°C) and rain drop impingement the coating must be able to withstand these environments without damage.

The objective of this program was to develop AR coatings for ZnS and GaAs which would meet the optical transmission requirements and at the same time survive the specified rainstorm and high temperature environments. The emphasis of this program was placed on the development of rain erosion resistant AR coatings. The selection and fabrication of coatings was based on Honeywell's experience in hardened coatings which meet Mil Spec humidity, adhesion and abrasion requirements, with the realization that coatings which meet these requirements are not necessarily rain erosion resistant.

The program included the following subtasks:

- Evaluation of candidate coatings materials
- Optimization of coating designs
- Fabrication of coatings on small ZnS and GaAs windows (1.5" x 0.5" x 0.2")
- Validating measurements
- Delivery of rain erosion samples to AFML for erosion resistance testing
- Coatings fabrication on large ZnS and GaAs windows (4" x 6" x 0.5") and delivery of one of each to AFML

Major program results can be summarized as follows:

1. Two layer coatings using ZnSe as the high index layer, and ThF_4, LaF_3 or NdF_3 as the low index layer on ZnS and GaAs windows, meet the optical transmission requirements at 1.06 μm (ZnS) between 8 μm and 10 μm (ZnS) and between 8 μm and 11 μm (GaAs).

2. The transmission requirements are not met in spectral regions where absorption of the window material is predominent, that is, between 0.5 μm and 0.9 μm, and between 10 μm and 10.5 μm for ZnS (the measured transmission of coated ZnS windows is between 85 and 90 percent) and between 11 μm and 12 μm for GaAs (the measured transmission of coated GaAs windows is between 85 and 90 percent).

3. Two layer coatings of $ZnSe/ThF_4$, $ZnSe/LaF_3$ and $ZnSe/NdF_3$ on ZnS passed rain erosion testing at AFML. The combination $ZnSe/NdF_3$ on ZnS was superior. The same layer combinations do not pass when prepared on GaAs windows applying identical fabrication process conditions used for ZnS. This finding may be related to the poor surface finish of GaAs substrates used for coatings preparation. The scratch and dig requirement of 60/40 was not met.

4. Measurements of transmission characteristics of coated ZnS substrates after rain erosion testing at AFML (over 20 minutes at 1 inch/hour simulated rainfall with relative drop impact velocities of 470 mph) showed transmission losses of about 10 percent with reference to transmission data taken before rain erosion testing. Samples with such small transmission losses after rain erosion testing were those which had scratch and dig characteristics close to 40/20 and which were post-annealed after coatings preparation.

5. The vacuum deposition of coatings was conducted at 343°C and post-annealing performed at 200°C in order to assure temperature stability of the coatings at 200°C.

The fabrication process of AR coating on IR windows and the identification of materials being used has been documented for the purpose of process control, process repeatibility, and high yields (~ 80 percent). This is essential for large quantity, large scale, low cost future production type programs.

Results of validating measurement on large coated windows will be presented as an addendum to this report.

SECTION II

CONCLUSIONS

Rain erosion resistance of double-layer thin-film antireflection coatings on ZnS IR windows has been demonstrated under conditions of 1 inch/hour rainfall, for 20 minutes, 1.8 mm drop diameter, and drop impact velocity of 470 mph.

The rain erosion resistance of coatings (being several micrometers thick) on ZnS can be achieved by selecting proper coatings materials such as NdF_3 (low index layer) and ZnSe (high index layer), by conducting the coatings fabrication at elevated substrate temperatures (343°C), by post-annealing (200°C) and by selecting window substrates which meet or exceed the scratch and dig window surface requirement of 60/40. The failure of the same coatings combinations to survive rain erosion testing when prepared on GaAs windows is attributed to the poor surface conditions of the GaAs windows.

SECTION III

RECOMMENDATIONS

Future programs shall emphasize high quality surface finish of window materials and impose a scratch and dig requirement of 40/20 as a design goal. This recommendation is based on results showing survival of coatings on high surface quality ZnS windows during rain erosion testing but showing severe degradation of the same coatings when prepared on GaAs, which has extremely poor surface qualities. ZnS windows, which have been scratched prior to coatings preparation, show accelerated coatings degradation during rain erosion testing in areas where the scratches were made.

SECTION IV

COATINGS PERFORMANCE GOALS

Coatings performance goals are defined by the contract and are summarized in Table 1.

Table 1. Performance Parameters and Goals

Performance Parameter	Goal
Optical Transmission	ZnS $\geq$ 60% 0.5-0.9 μm $\geq$ 60% 1.06 μm $\geq$ 95% 8-10.5 μm GaAs 95% 8-12 μm
Rain Erosion	No removal of coatings when tested under the following conditions: Rainfall: 1 inch/hr Drop diameter: 1.8 mm Impact Velocity: 470 mph Duration: $\geq$ 20 min
Temperature Stability	No performance degradation at 200°C and -55°C

SECTION V

IR WINDOW MATERIALS

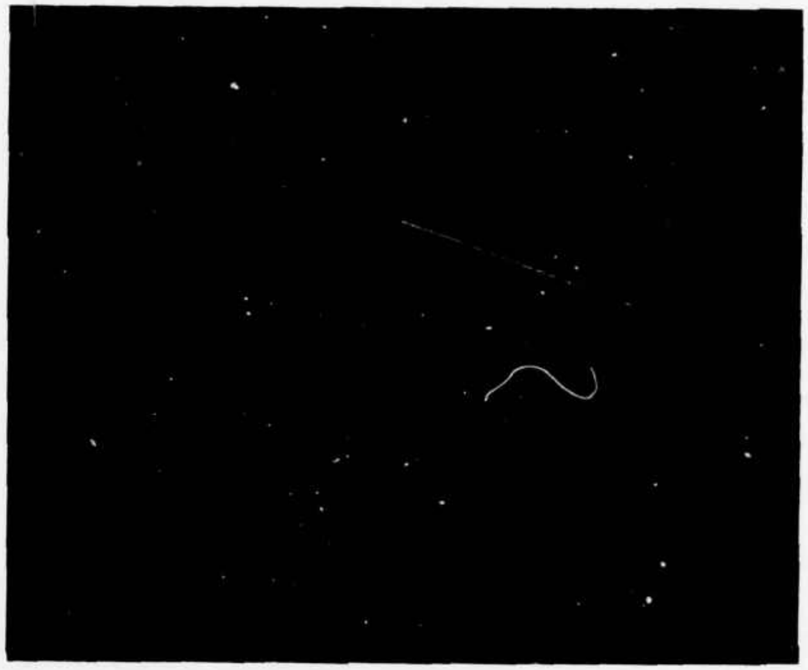
ZINC SULFIDE

Raw sample window substrates of ZnS (1.5" x 0.5" x 0.2") were purchased from the Raytheon Company. They were polished at the PTR Optics Company to meet the following specifications:

- Flatness: 1λ in visible
- Parallelism: 3 minutes
- Scratch, dig and surface finish: 60/40
- Edge rounded to 0.08"

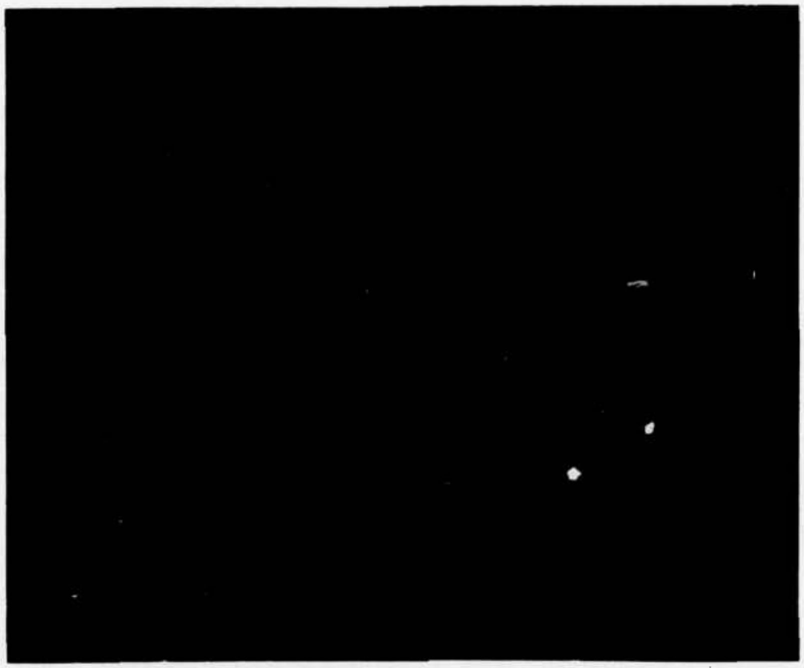
The large ZnS window (6" x 4" x 0.5") was ordered from the same vendors to meet the above requirements except that the parallelism specification was 20 arc seconds. Receiving inspection at Honeywell showed that the scratch and dig requirement of 60/40 was not met while the other parameters were within specification. A photo of a representative surface area is shown in Figure 1. Additional substrates of ZnS were polished by Advanced Materials Fabrication Optics Company, Woburn, MA. These samples exceeded the scratch and dig requirement and were typically 40/20. A photo of a representative surface area is shown in Figure 2.

The optical transmission of ZnS window samples, as received, was measured between 0.4 and 14 μm. Results are shown in Figures 3 and 4. Figure 3 shows that the short wavelength absorption edge is shifted from 0.34 μm (expected for intrinsic ZnS) to approximately 0.8 μm. This is very likely due to excess zinc and/or impurities and the polycrystalline nature of the ZnS window substrates.



Magnification: 100x

Figure 1. Representative Area of ZnS Window as Received, Which Does Not Meet 60/40 Scratch and Dig Requirement



Magnification: 100x

Figure 2. Representative Area of ZnS Window as Received, Which Exceeds 60/40 Scratch and Dig Requirement

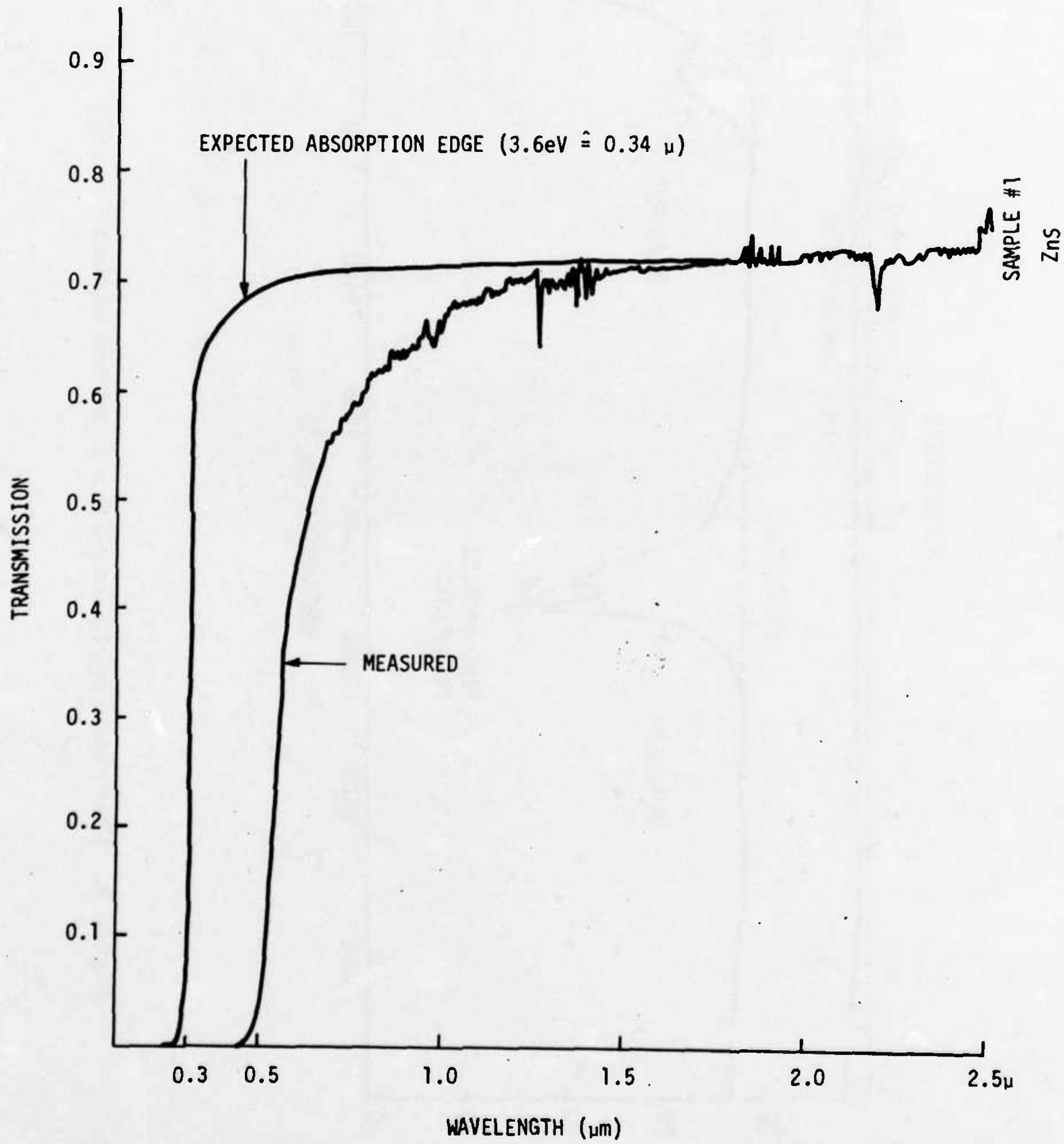


Figure 3. Short Wavelength Absorption Edge of ZnS Window as Received

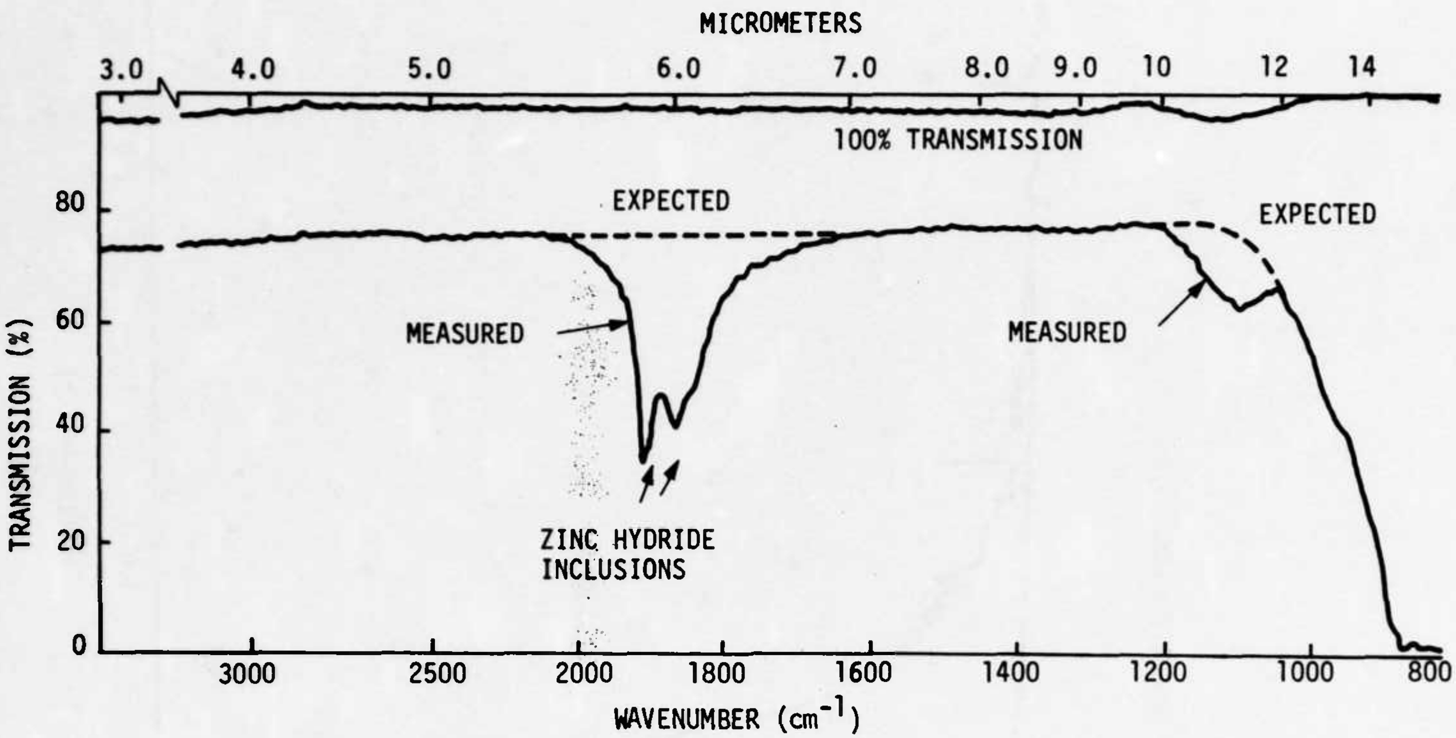
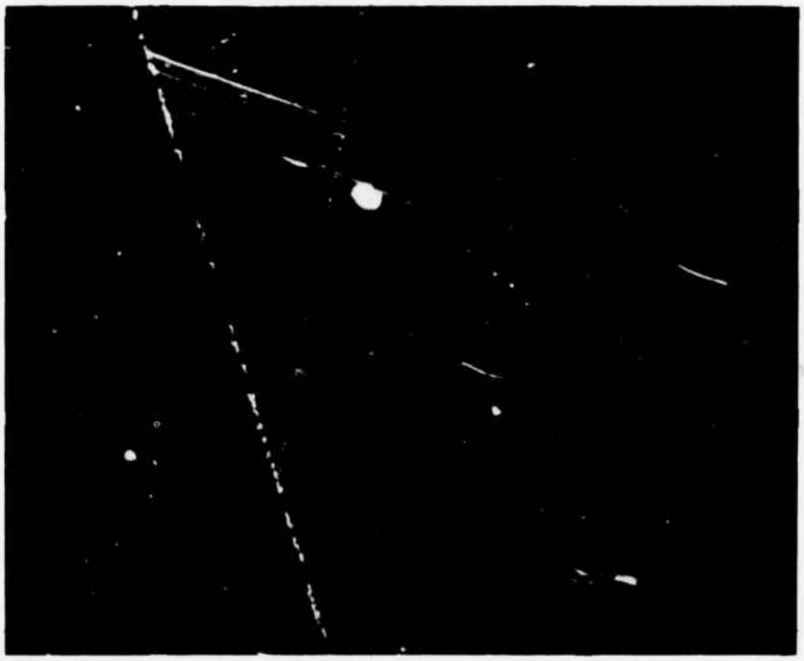


Figure 4. Transmission of Zinc Sulfide Substrate without Coatings

The two transmission minima at approximately 6 μm (Figure 4) are very likely due to inclusions of zinc-hydride (according to Raytheon). Except for these two transmission disruptions the average transmission between 1.5 μm and 10 μm is about 75 percent. The long wavelength roll-off of the spectral transmission characteristics, shown in Figure 4, starts at about 10 μm. The expected roll-off should start at about 10.8 μm. Due to high window absorption at wavelengths less than 0.8 μm and larger than 10 μm, the transmission goals for coated ZnS sulfide windows were not met between 0.5 μm and 0.9 μm and between 10.0 μm and 10.5 μm.

GALLIUM ARSENIDE

Small polished substrates of GaAs (1.5" x 0.5" x 0.2") and a large sample (6" x 4" x 0.5") were received from AFML. None of the GaAs samples met the scratch and dig requirement of 60/40. A photo of a representative surface area is shown in Figure 5. Typical transmission characteristics of the GaAs samples, as received, are shown in Figures 6 and 7 for the wavelength range between 0.5 μm and 12 μm. Figure 6 shows that the short wavelength absorption edge is shifted toward longer wavelengths. The long wavelength transmission roll-off shown in Figure 7 starts at about 11.8 μm. The average transmission between 2.0 μm and 11.5 μm is approximately 60 percent.



Magnification: 100x

Figure 5. Representative Area of GaAs Window as Received, Which Does Not Meet 60/40 Scratch and Dig Requirement

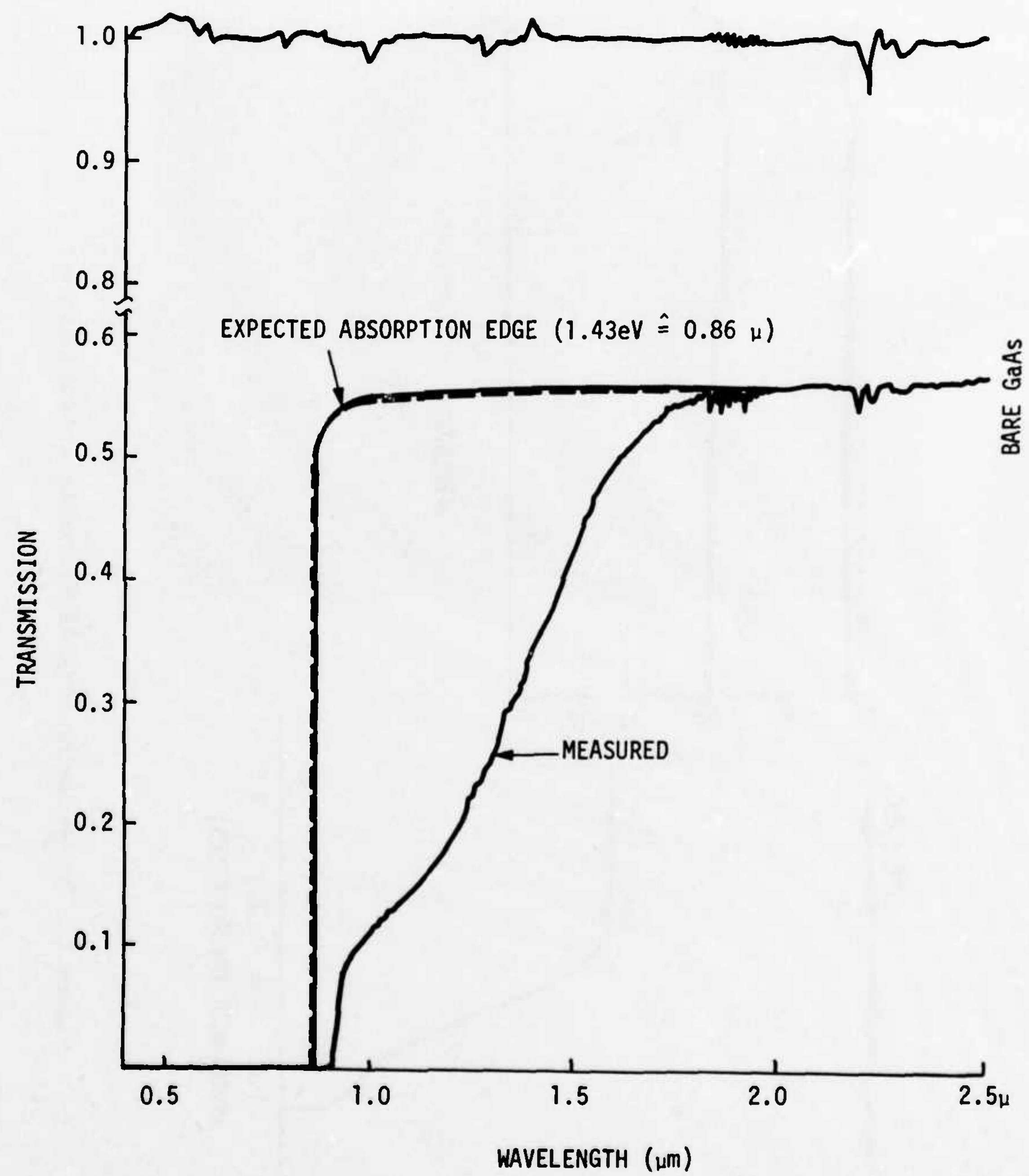


Figure 6. Transmission of GaAs Substrate without Coatings

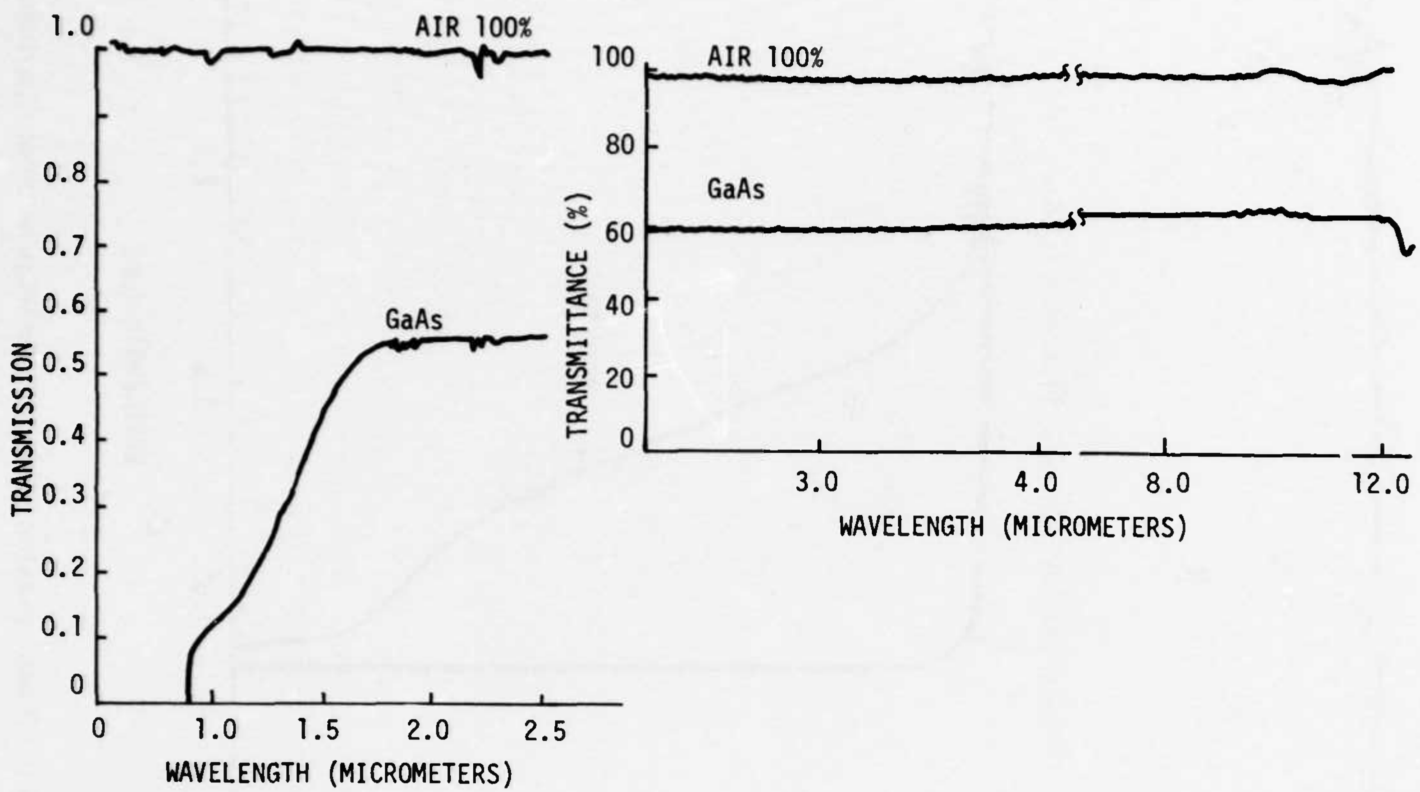


Figure 7. Transmission of GaAs Substrate without Coatings

SECTION VI

ANTIREFLECTION COATING DESIGNS

The antireflective coating design for gallium arsenide (GaAs) infrared window material must be at least 95 percent transmitting over the 8 to 12 μm wavelength region. The simplest AR coating design would be a single-layer coating with a refractive index n_1 satisfying the following equation:

$$n_1 = (n_o n_s)^{1/2} \qquad (1)$$

where n_o is the index of the incident medium and n_s(= 3.14) is the index of the GaAs window. The thickness of the layer must be an odd multiple of a quarter wave at the design wavelength. A single layer of a material with an index equal to

$$n_1 = \sqrt{3.14} = 1.77$$

and of thickness t = 1.411 μ would produce a zero reflectance at λ = 10 μm. However, the increase in reflectance with variation of λ away from 10 μm is too large to meet the program requirements. Figure 8 displays the calculated transmission versus wavelength of such a single-layer coating on a GaAs surface. The reflection losses of two such coated surfaces would be greater than 5 percent at both 8 μm and 12 μm.

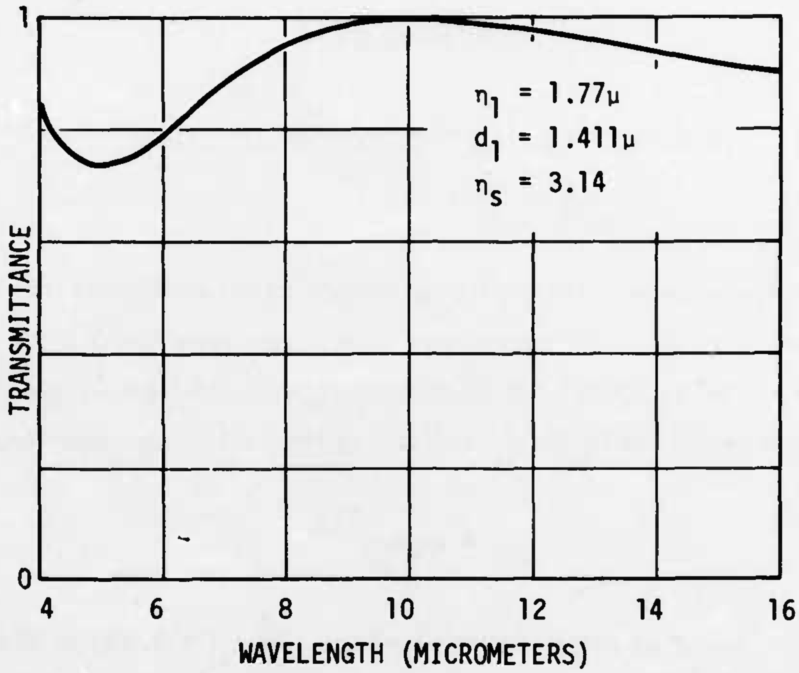


Figure 8. Calculated Transmission of a GaAs Surface with a Single-Layer AR Coating

A broader region of low reflectance can be achieved using double-layer anti-reflection coatings. If n_1 and n_2 are the refractive indices of the outer and inner layers, respectively, then the values of n_1 and n_2 for which suitable adjustment of film thicknesses can produce zero reflectance are defined by a Schuster diagram. A Schuster diagram for double-layer AR coatings on GaAs is shown in Figure 9. Refractive index combinations (n_1, n_2) that fall on the line defined by

$$n_2 = n_1(n_s/n_o)^{1/2} \quad (2)$$

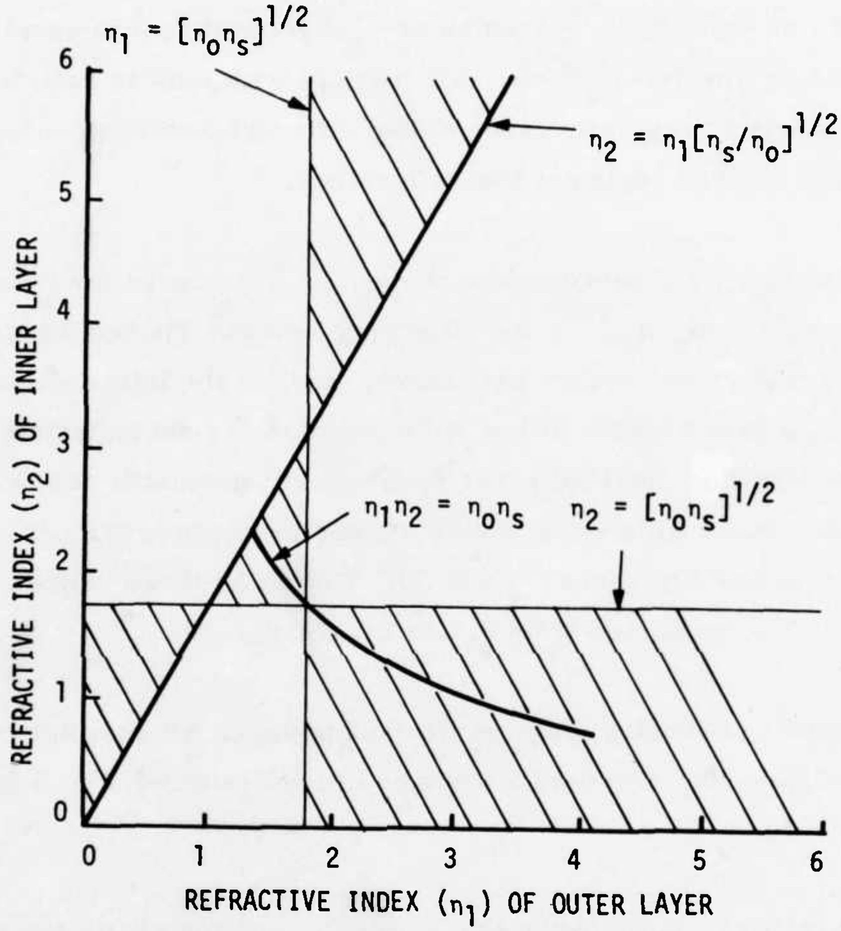


Figure 9. Schuster Diagram for Double Layer AR Coatings on GaAs [AR Coatings designs exist for points (n_1, n_2) in the hatched areas.]

represent the special case where each layer is $\lambda/4$ thick. Combinations (n_1, n_2) that fall on the curve defined by

$$n_1 n_2 = n_o n_s \tag{3}$$

have layers of equal thickness which are, in general, not integral multiples of one-quarter wavelength thick. AR coatings with indices satisfying Equation (3) produce a zero reflectance at two different wavelengths and therefore provide a broad region of low reflectance.

As the point (n_1, n_2) is moved along the $n_1 n_2 = n_o n_s$ curve towards the line defined by $n_2 = n_1 (n_s / n_o)^{1/2}$, the difference between the two wavelengths at which zero reflectance occurs decreases; and, at the intersection of the two curves, a broad region of low reflectance with zero reflectance at a single wavelength is obtained. The program requirements can be satisfied with a double layer AR coating whose indices lie close to the point defining the intersection of Equations (2) and (3). For GaAs these indices can range from 1.3 to 1.7 for n_1 and from 2.3 to 2.6 for n_2.

A corresponding Schuster diagram for double-layer AR coatings on ZnS is shown in Figure 10. The critical ranges of indices are 1.0-1.6 for n_1 and 1.5-2.4 for n_2.

A large variety of coating candidate materials was originally examined based on qualifying refractive indices. Coatings combinations which were selected and actually fabricated on GaAs and ZnS windows are listed as follows:

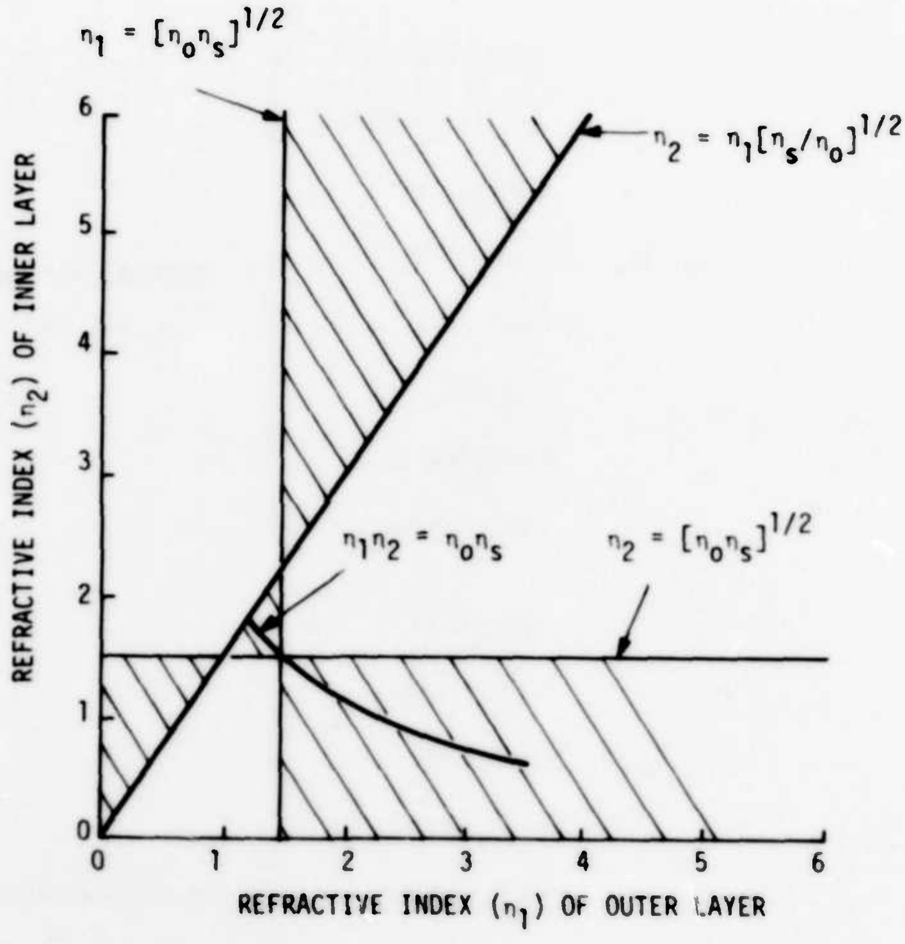


Figure 10. Schuster Diagram for Double-Layer AR Coatings on ZnS [AR Coating designs exist for points (n_1, n_2) in the hatched areas.]

Outer Layer	Inner Layer
n_1 = 1.0-1.7	n_2 = 1.5-2.6

$ThF_4/ZnSe$
$Na_3AlF_6/ZnSe$
$CaF_2/ZnSe$
ThF_4/TlI
CaF_2/TlI
Na_3AlF_6/TlI
$LaF_3/ZnSe$
$NdF_3/ZnSe$

on GaAs substrates $n_s = 3.14$

$ThF_4/AgCl$
$CaF_2/AgCl$
CaF_2/TlI
$ThF_4/ZnSe$
$LaF_3/ZnSe$
Si
ZnSe
LaF_3
$LaF_3/Si/LaF_3$
$NdF_3/ZnSe$

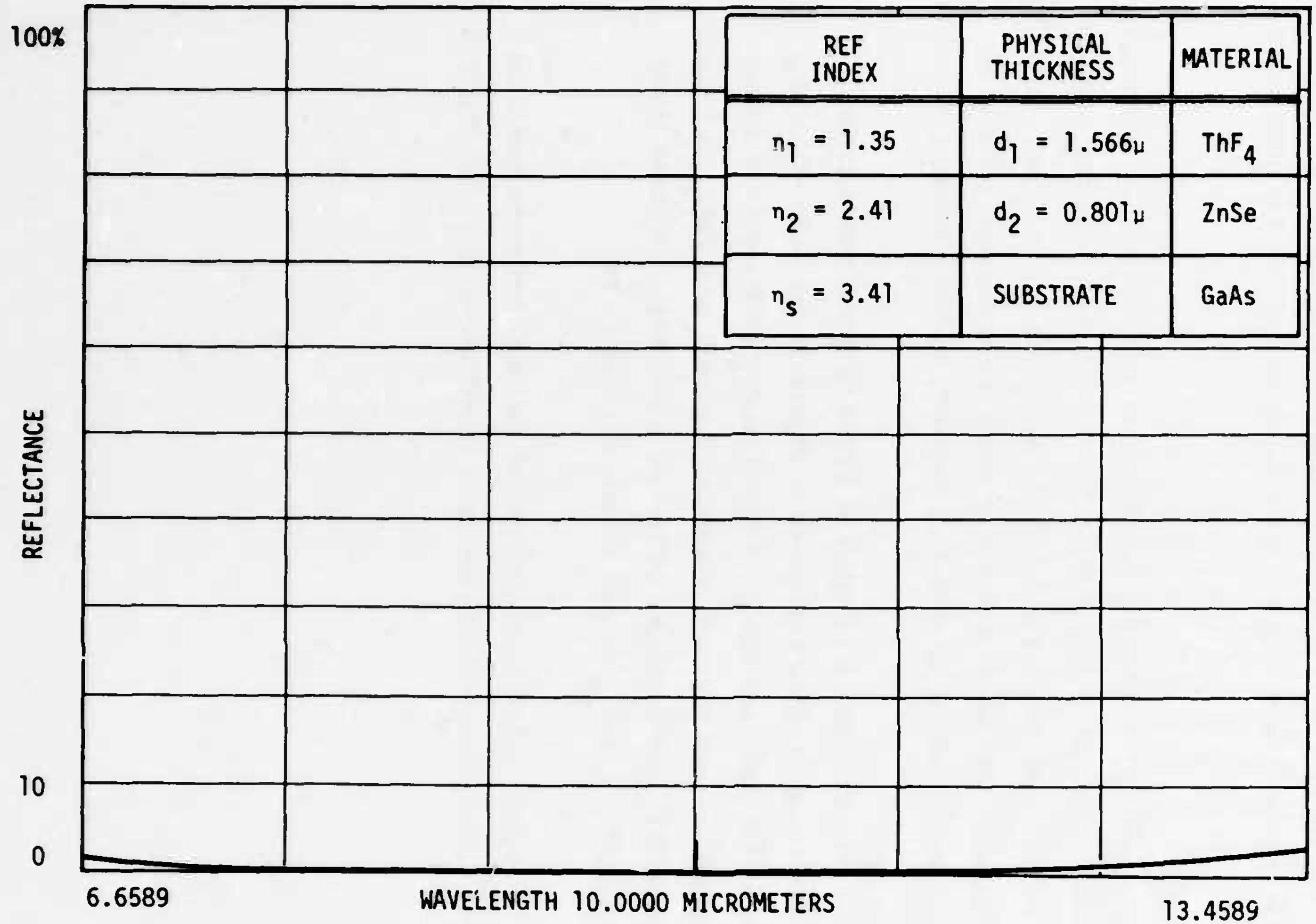
on ZnS substrates $n_s = 2.26$

Evaluation of transmission and reflectance characteristics of coated test samples demonstrated general agreement between calculated and measured data.

Failures during testing for adhesion, solubility in water, humidity resistance, and rain erosion resistance reduced the original materials candidates proposed to the following coating materials: Si, NdF_3, LaF_3, ThF_4 and ZnSe. These materials became the prime coating material candidates because of their demonstrated durability to abrasion, humidity and rain erosion.

The calculated reflectance as a function of wavelength for double-layer coatings combinations on GaAs are shown in Figure 11 for ZnSe and ThF_4, and in Figure 12 for ZnSe and NdF_3. The calculated reflectance of double layer coatings on ZnS are shown in Figure 13 for NdF_3 and ThF_4, in Figure 14 for ZnSe and LaF_3 and in Figure 15 for ZnSe and NdF_3. A three layer combination of $LaF_3/Si/LaF_3$ on ZnS is shown in Figure 16.

A summary of refractive index, coefficient of thermal expansion and transmission limits of the prime coating material candidates is shown in Table 2.



REF INDEX	PHYSICAL THICKNESS	MATERIAL
$n_1 = 1.35$	$d_1 = 1.566\mu$	ThF_4
$n_2 = 2.41$	$d_2 = 0.801\mu$	ZnSe
$n_s = 3.41$	SUBSTRATE	GaAs

Figure 11. Computer Printout of Reflectance of Double Layer Coating of ThF_4/ZnSe on GaAs

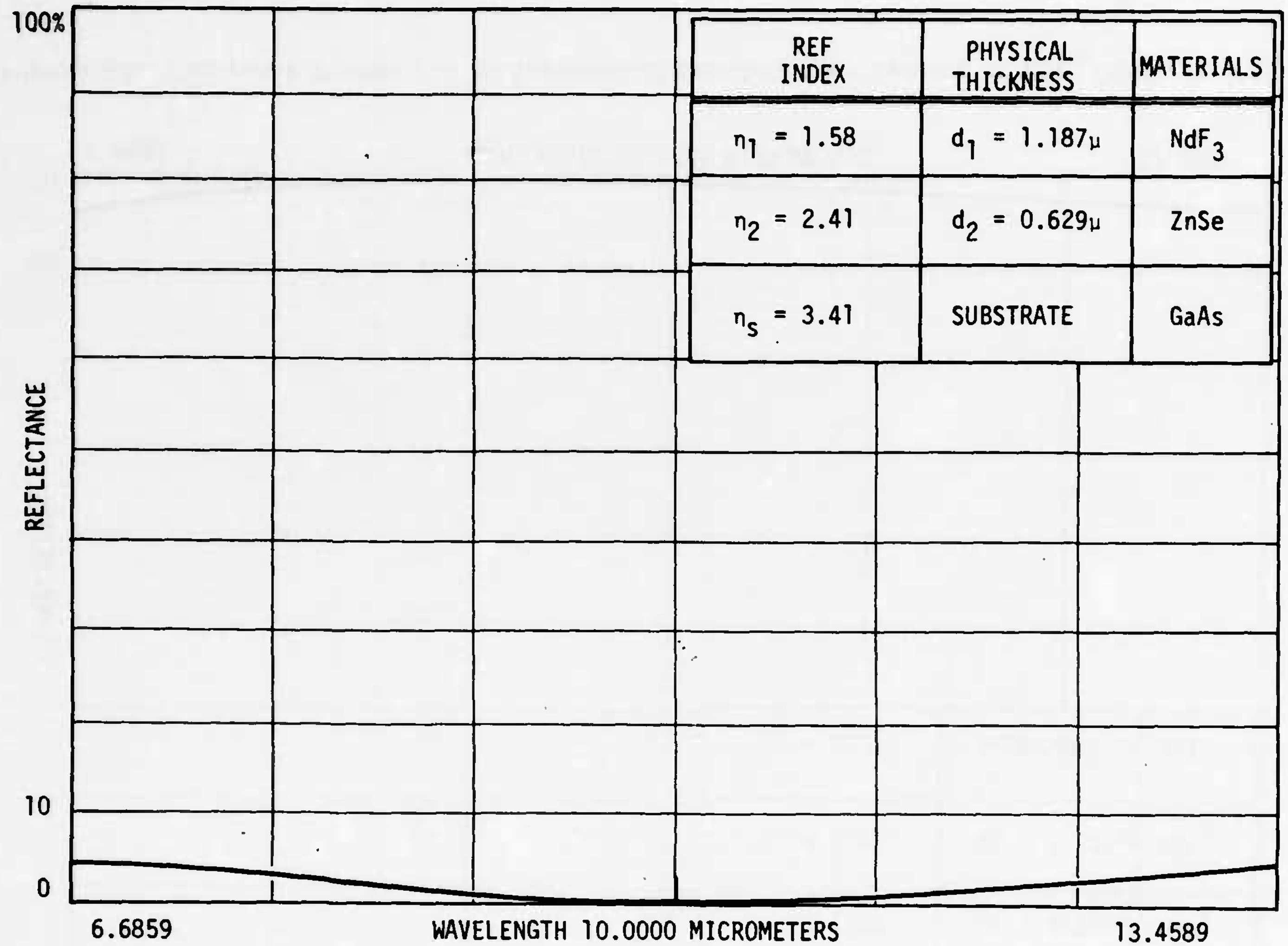


Figure 12. Computer Printout of Reflectance of Double Layer Coating of NdF_3/ZnSe on GaAs

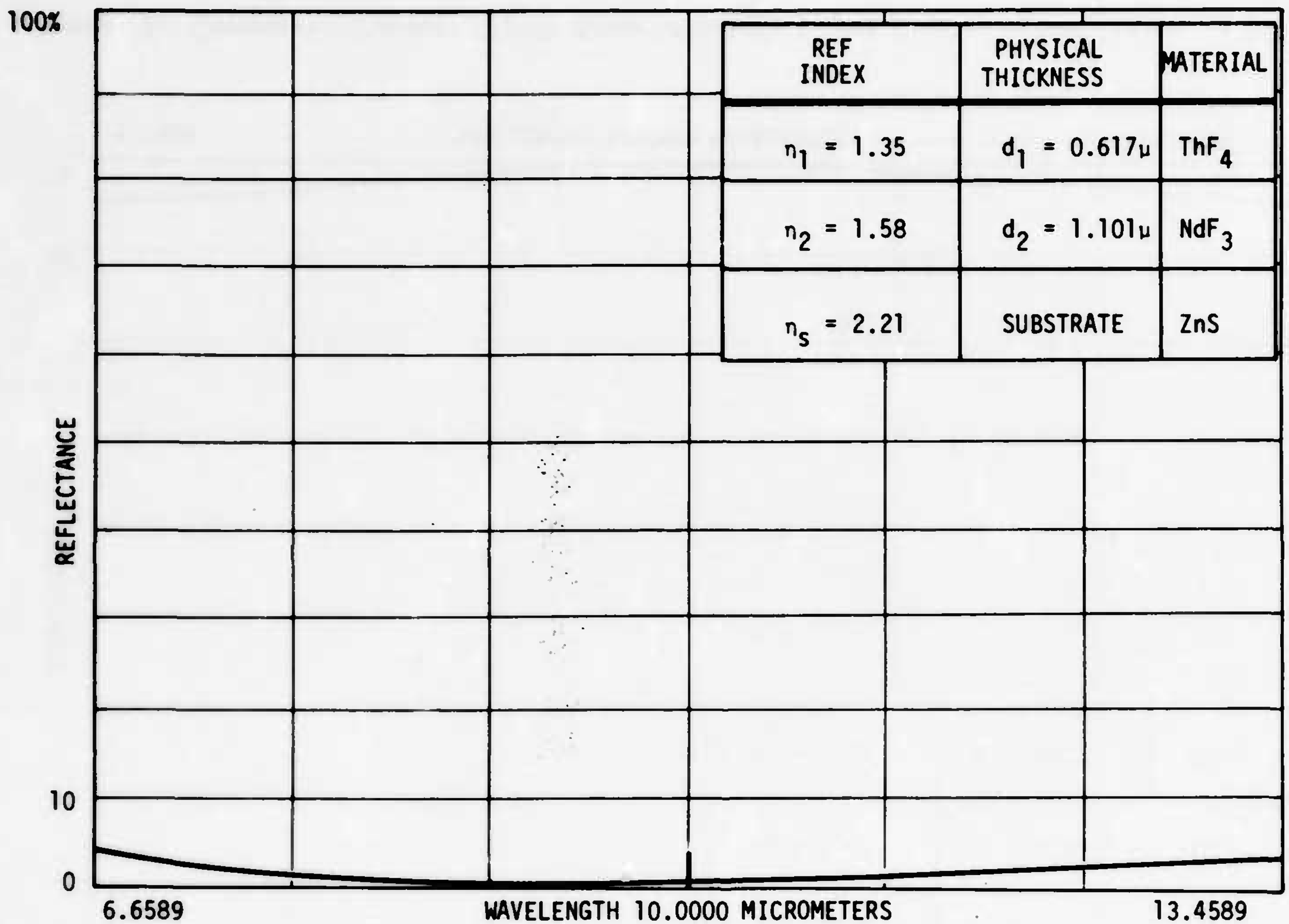


Figure 13. Computer Printout of Reflectance of Double Layer Coating of ThF_4/NdF_3 on ZnS

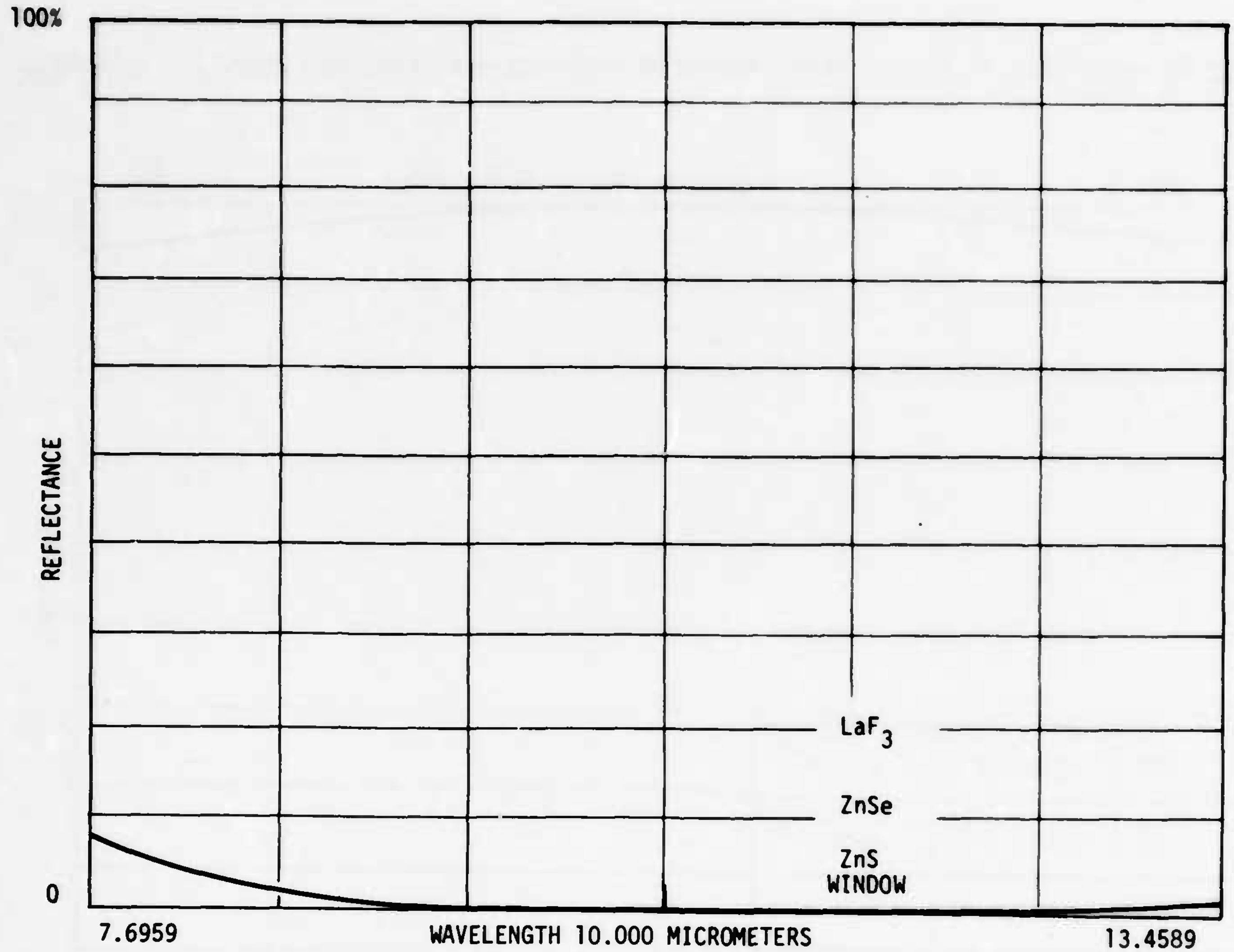


Figure 14. Computer Printout of Reflectance of Double Layer Coating of LaF_3/ZnSe on ZnS

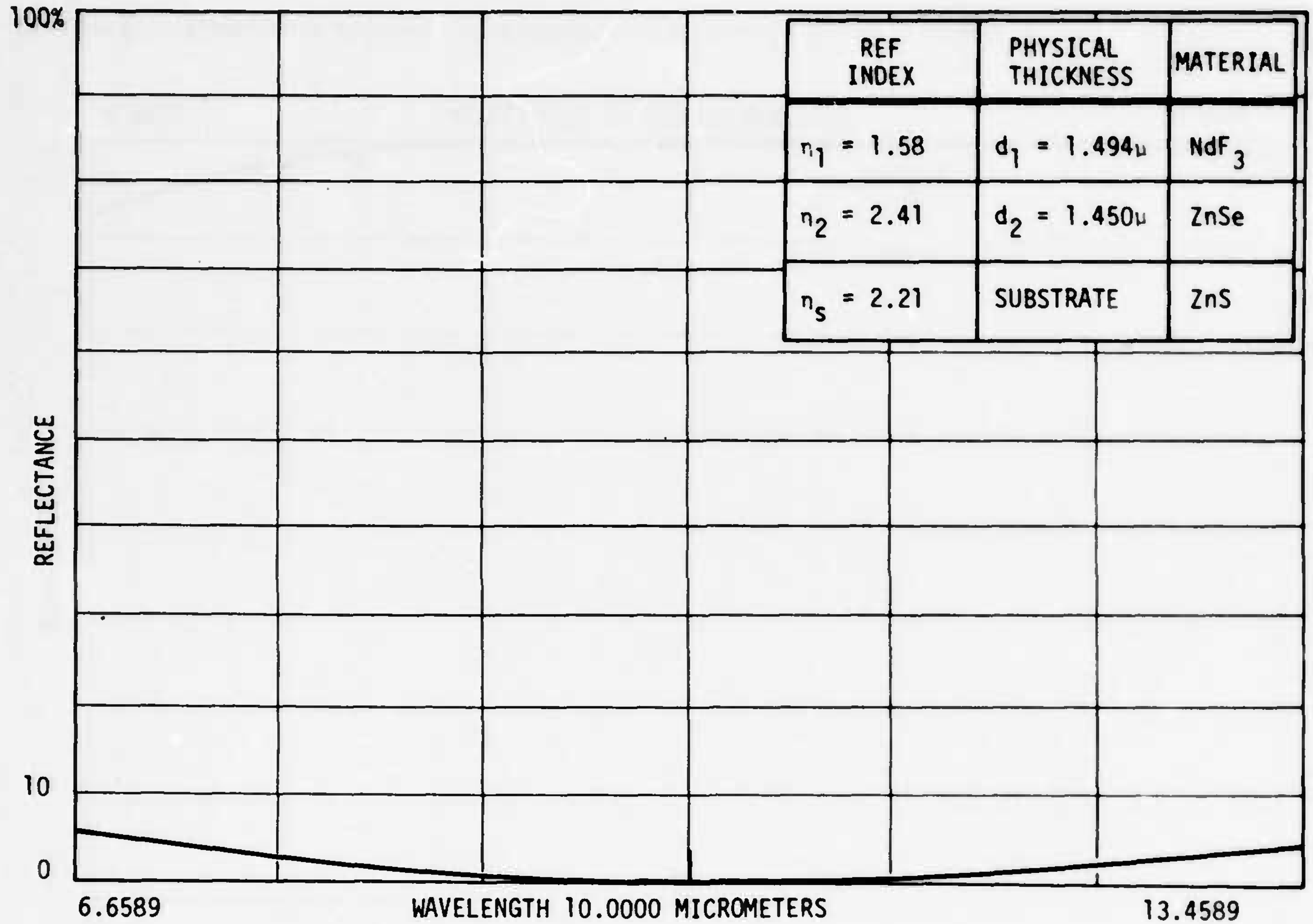


Figure 15. Computer Printout of Reflectance of Double Layer Coating of NdF_3/ZnSe on ZnS

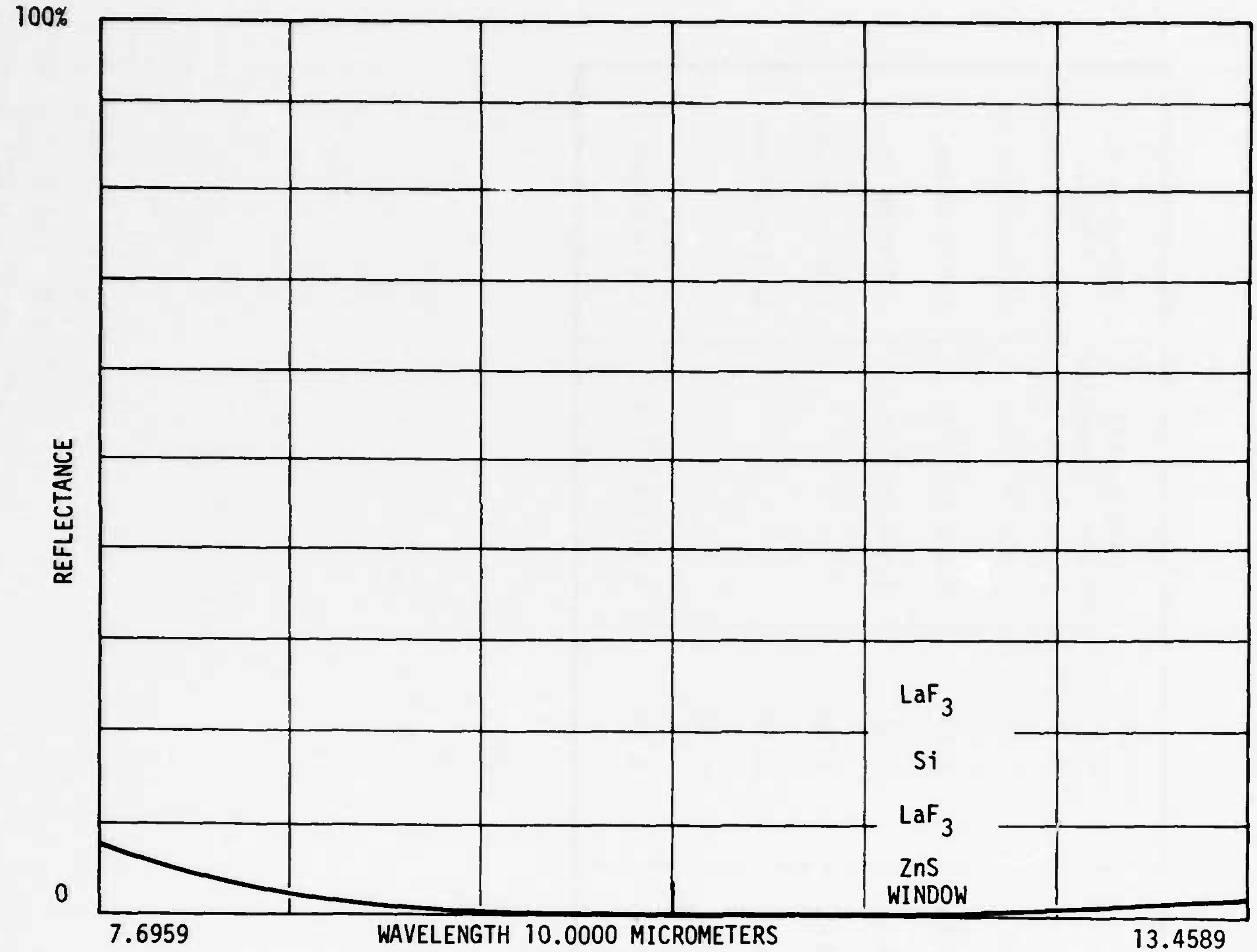


Figure 16. Computer Printout of Reflectance of a Three-Layer Coating of $LaF_3/Si/LaF_3$ on ZnS

Table 2. Summary of Refractive Index, Coefficient of Thermal Expansion and Transmission Limits of Prime Coating Material Candidates

Material	Refractive Index n @ 10 μm	Coefficient of Thermal Expansion	Transmission Limits
ZnS	2.26	6.3×10^{-6}/°C	0.35 to 14.5 μm
GaAs	3.14	5.7×10^{-6}/°C	1.0 to 15 μm
ZnSe	2.41	7.7×10^{-6}/°C	0.5 to 20 μm
ThF_4	1.35		0.26 to 12 μm
LaF_3	1.57		0.13 to 13 μm
NdF_3	1.58		
Si	3.42	4.15×10^{-6}/°C	1.2 to 15 μm

SECTION VII

COATINGS FABRICATION

The preparation of coatings on ZnS and GaAs substrates was performed using the electron beam vacuum deposition technique. The process is documented for ZnS and is presented in the Appendix. Major variables of the coatings preparation were:

- Surface cleaning of substrates
- Purity and pre-conditioning of source materials for vacuum deposition
- Pressure during deposition
- Substrate temperature during deposition
- Deposition rate
- Coatings thicknesses
- Duration, temperature and environment of post-annealing
- Temperature versus time profile during cooling
- Cleanliness of deposition and post-annealing facilities

Process control was maintained by monitoring substrate temperature, deposition rate, vacuum pressure, coating thickness and by following step by step the process in the Appendix. Deviations from the process procedures were recorded in a log book. Materials are identified according to vendor, Lot No., grade identification, and impurity content. All coatings were prepared from identical source materials.

Using Honeywell's computer program for optical coatings design, the physical thickness of each layer was calculated for optimum transmission and reflectance characteristics. Calibration of physical thickness, versus frequency shift of the quartz crystal thickness monitor in the deposition chamber, was carried out. The physical thickness of coatings on test samples was measured using a Sloan Angstrometer.

SECTION VIII

OPTIMIZATION OF FABRICATION PROCESS AND COATINGS DESIGN

Optimization of the coatings design was conducted primarily by

- Selection of coating materials which passed rain erosion testing
- Adjustment of physical layer thicknesses to provide optimum optical transmission characteristics over the required spectral ranges
- Selection of sufficiently high substrate temperature during vacuum deposition and post-annealing in order to provide a high degree of layer crystallinity, good adhesion, sufficient temperature stability and enhanced rain erosion resistance.

Representative transmission and reflectance spectra of optimized two layer coatings on ZnS and GaAs window samples are shown in Figures 17 through 22. These figures are:

Figure 17. Transmission of Coated ZnS Windows between 0.5 and 2.5 μm

Figure 18. Transmission and Reflectance of Coated ZnS ($ZnSe/NdF_3$) Before and After Post-Annealing

Figure 19. Transmission and Reflectance of Coated ZnS ($ZnSe/ThF_4$)

Figure 20. Transmission and Reflectance of Coated ZnS ($ZnSe/LaF_3$)

Figure 21. Transmission and Reflectance of Coated GaAs ($ZnSe/NdF_3$)

Figure 22. Transmission and Reflectance of Coated GaAs ($ZnSe/ThF_4$)

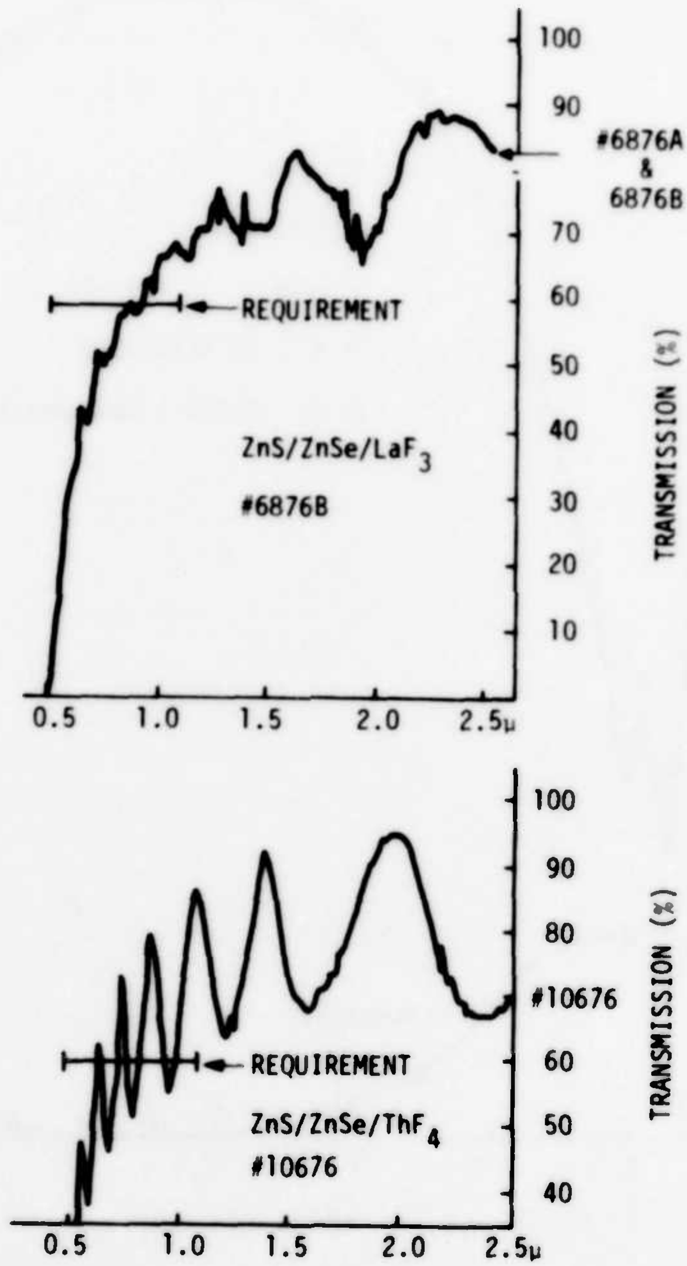


Figure 17. Transmission of Coated ZnS Windows between 0.5 and 2.5 μm

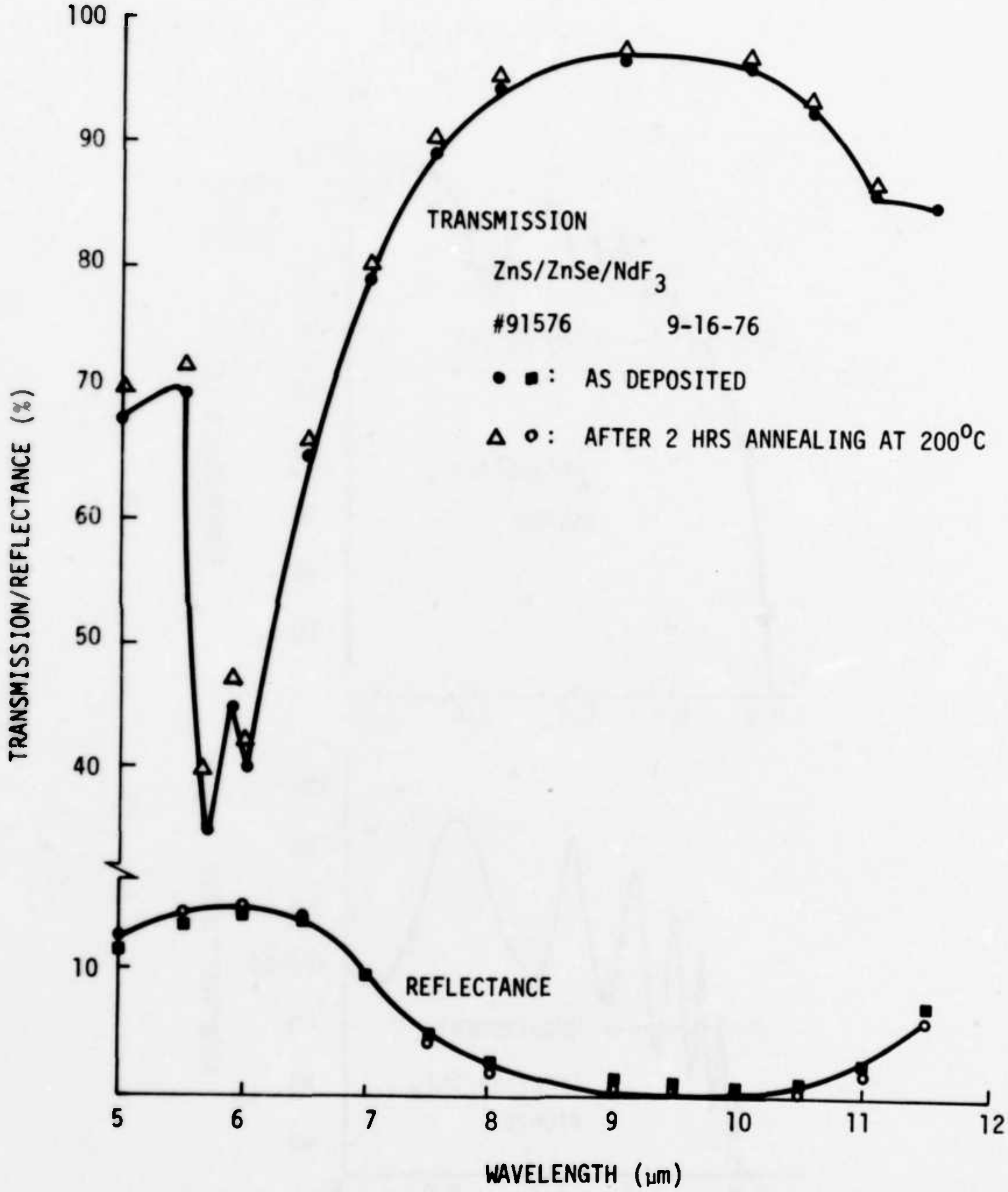


Figure 18. Transmission and Reflectance of Coated ZnS ($ZnSe/NdF_3$) Before and After Post-Annealing

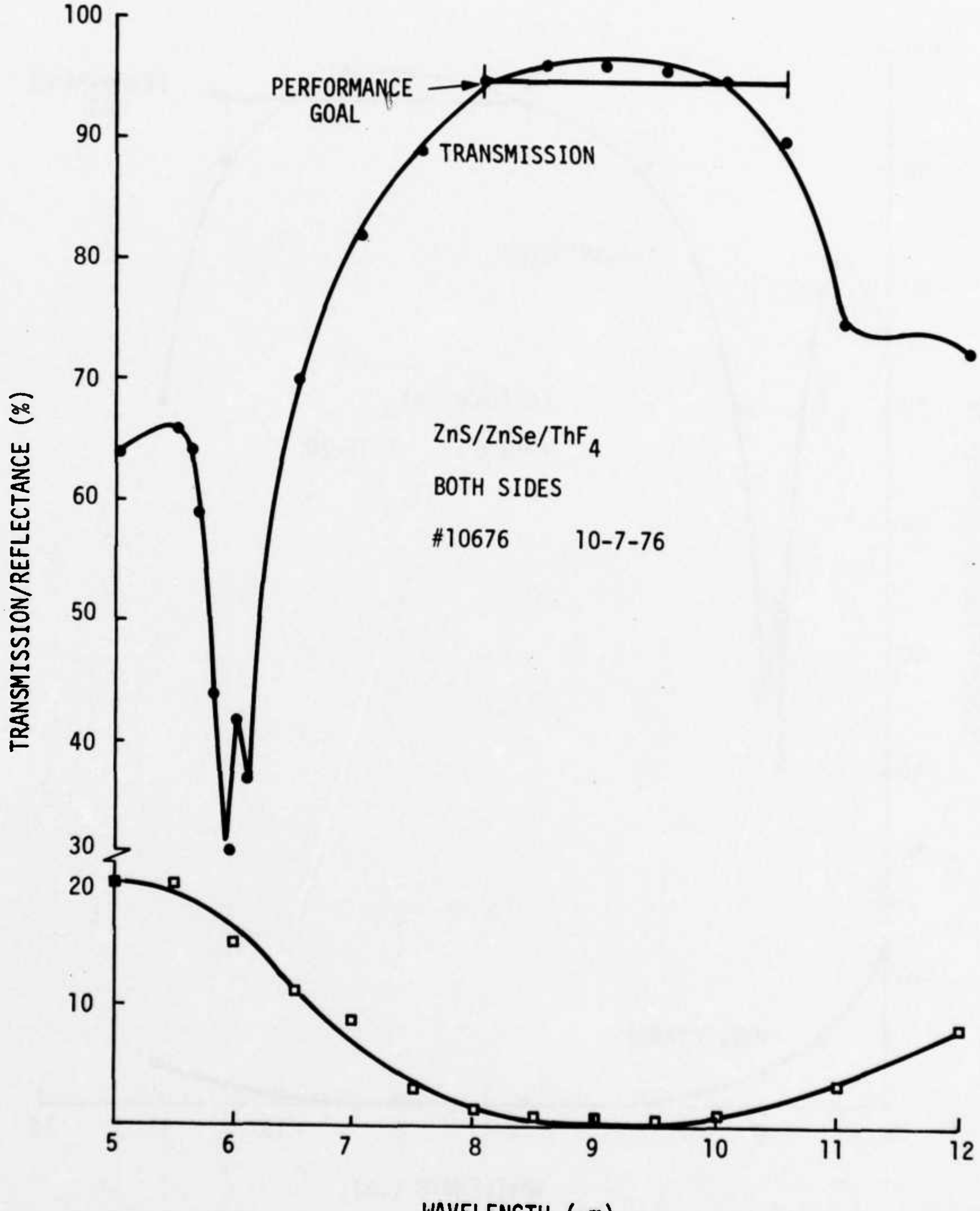


Figure 19. Transmission and Reflectance of Coated ZnS (ZnSe/ThF_4)

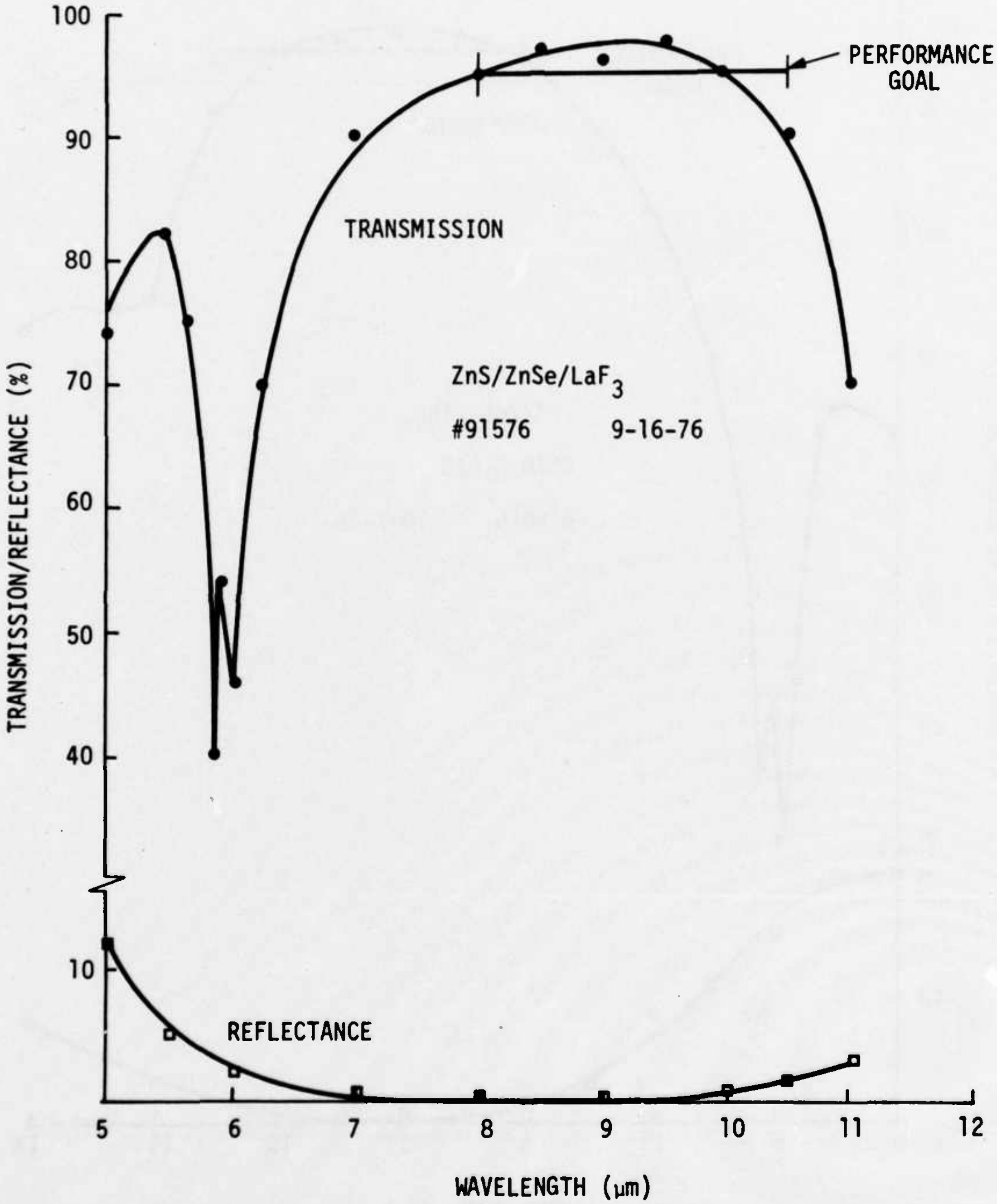


Figure 20. Transmission and Reflectance of Coated ZnS ($ZnSe/LaF_3$)

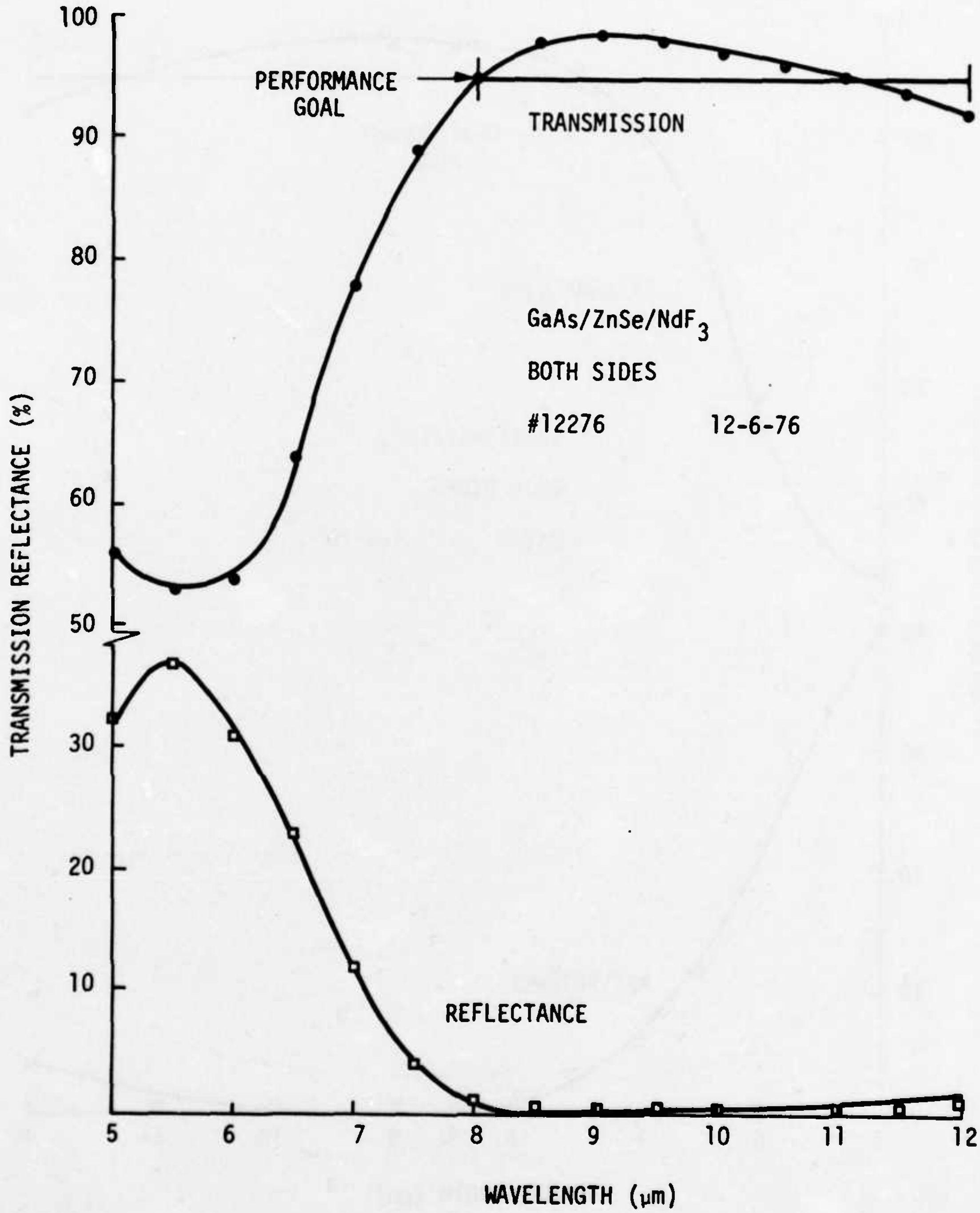


Figure 21. Transmission and Reflectance of Coated GaAs ($ZnSe/NdF_3$)

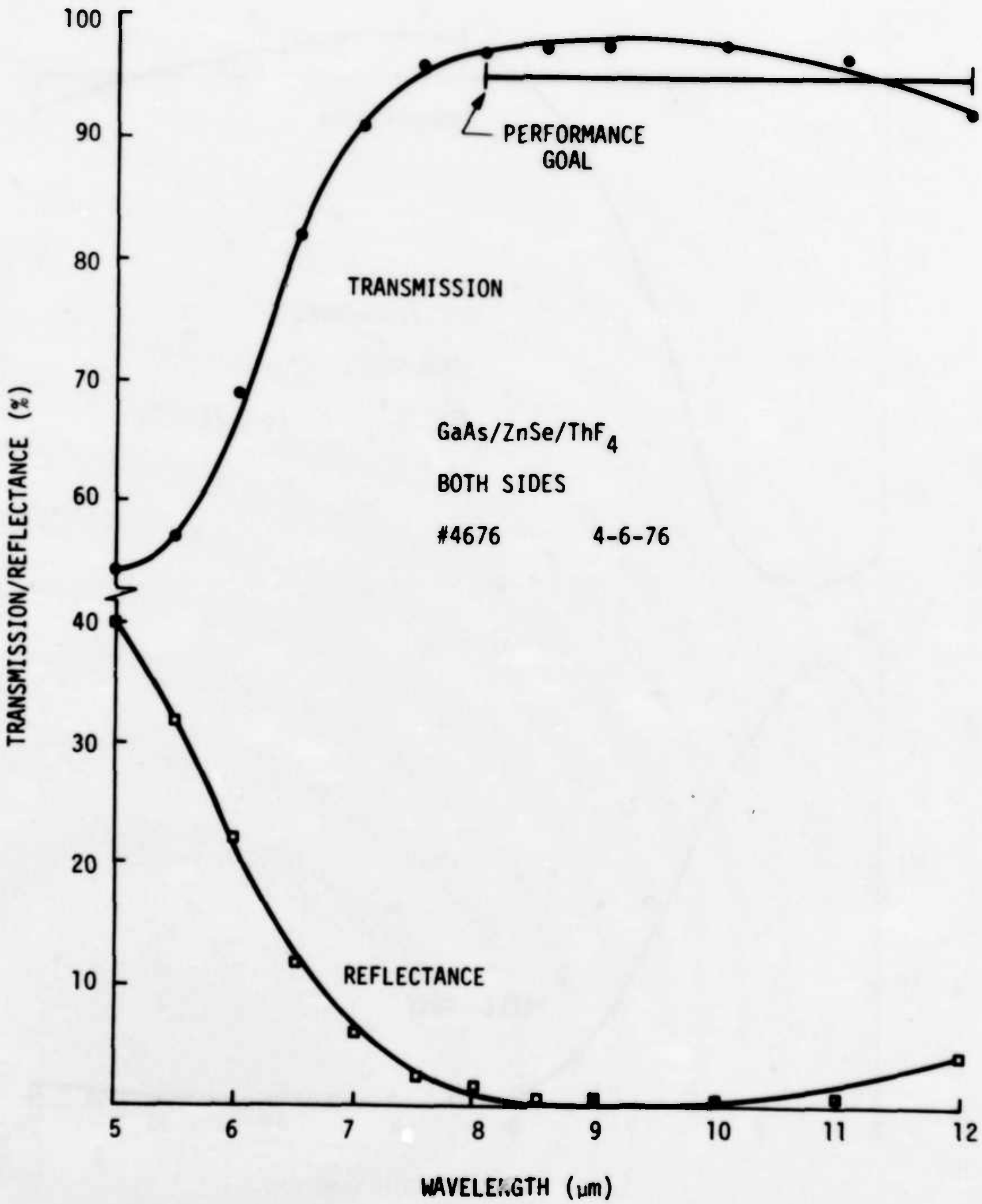


Figure 22. Transmission and Reflectance of Coated GaAs ($ZnSe/ThF_4$)

SECTION IX

OPTICAL PERFORMANCE OF COATED WINDOWS VERSUS PERFORMANCE GOALS

The optical performance of coated ZnS and GaAs substrates versus performance goals is summarized in Table 3.

Table 3. Optical Performance of Coated Windows versus Design Goals

Requirements	ZnS	GaAs
≥ 60 percent transmission; 0.5-0.9 μm	Met at 0.9 μm; not met at <0.9 μm due to substrate absorption.	Not applicable.
≥ 60 percent transmission; 1.06 μm	Met	Not applicable.
≥ 95 percent transmission; 10.6 μm	Met at 8-10 μm; 85-90 percent at 10.5 μm due to substrate absorption.	Not applicable.
≥ 95 percent transmission; 8-12 μm	Not applicable.	Met at 8-11 μm; 85-90 percent at 11-12 μm due to substrate absorption.

ZINC SULFIDE WINDOWS

Data (Figures 17 through 20) show 62 percent transmission at 0.9 μm and 1.06 μm and 95-97 percent in the range between 8 μm and 10 μm. This means that the performance goal for optical transmission is met at 0.9 μm, 1.06 μm and in the wavelength range from 8 μm to 10 μm. The performance goal is not met in the wavelength region between 0.5 μm and 0.85 μm due to the shift of the absorption edge of the ZnS windows from 0.34 μm (expected in intrinsic ZnS) to 0.8 μm (see Figure 3). This shift is very likely due to excess zinc and/or impurities and the polycrystalline nature of the ZnS substrate. The transmission between 10.0 μm and 10.5 μm is between 85 and 90 percent and does not meet the program performance goal. The reduced transmission is again due to substrate absorption. As shown in Figure 4 the substrate transmission starts to roll-off at 10 μm and not at 10.8 μm as one would expect in pure ZnS.

GALLIUM ARSENIDE WINDOWS

Data (Figures 21 and 22) show 95-98 percent transmission in the wavelength range between 8 μm and 11.0 μm which meets the program performance goal. The program goal is not met between 11 and 12 μm due to substrate absorption. The transmission of the coated samples drops to about 90 percent between 11 and 12 μm.

SECTION X

RAIN EROSION TEST DATA

Coated window samples of ZnS and GaAs (1.5" x 0.5" x 0.2") were delivered to AFML according to the delivery plan of the contract. The rain erosion testing was conducted by AFML/MBE. The test facility simulates rainfall of 1 inch/hour with an average raindrop diameter of 1.8 mm and a raindrop impact velocity of 470 mph. The variable is the exposure time to the above specified rainfall conditions. The program goal was to withstand a minimum exposure time of 20 minutes. Results of the rain erosion testing were recorded by AFML and submitted to Honeywell. This rain erosion data is presented in Tables 4, 5 and 6. Significant results of the rain erosion testing can be summarized and interpreted as follows:

1. In reference to sample AFML numbers 7189, 7548, 7549, 7550, 7552 and 7553, coating combinations of ThF_4/ZnSe, LaF_3/ZnSe and NdF_3/ZnSe on ZnS met the rain erosion resistance goal. The rain erosion resistance of the combination NdF_3/ZnSe was superior in that it survived an exposure time of 30 minutes.

2. The same coating combinations on GaAs did not meet the rain erosion resistance requirements as demonstrated with samples number 7185, 7437, 7438 and 7551.

Table 4. Rain Erosion Data--1 Inch/Hour Simulated Rainfall (1.8 mm Diameter Drops)

AFML No.	Coating Material (Outside Layer Listed First)		Substrate	Exposure Time at 470 mph (min)	Comments
6999	LaF_3	(500°F)	ZnS	0.4	Coating completely removed.
7000	LaF_3	(250°F)	ZnS	---	Not run. Film flaked off during exposure of other side.
7001	ZnSe	(250°F)	ZnS	---	Not run.
7002	ZnSe	(500°F)	ZnS	30.4	Ring type fractures in coating and substrate. Coating removed only in very small areas along surface cracks.
7003	LaF_3/ZnSe	(250°F)	ZnS	---	Not run.
7004	LaF_3/ZnSe	(500°F)	ZnS	0.5	Several large areas and many small spots of coating removal. LaF_3 may be removed completely by 0.3 minutes.
7005	ThF_4/ZnSe		ZnS	0.1	Coating completely removed in some spots. One layer still visible in some areas.
7006	Si		ZnS	30.0	Ring type fractures in coating and substrate. Coating removed along surface cracks but most of coating remains.
7007	LaF_3/Si/LaF_3		ZnS	0.4	Coating completely removed.
7008	LaF_3/ZnSe		ZnS	---	Not run. Coating flaked during exposure of other side.
7009	LaF_3/ZnSe		ZnS	0.1	Small isolated spots of coating removal.
7010	ThF_4/ZnSe		GaAs	---	Not run. Coating coming off before exposure.
7011	ThF_4/ZnSe		GaAs	---	Not run. Coating coming off before exposure.
7012	ThF_4/ZnSe		ZnS	0.1	ThF_4 almost completely removed. Small areas where ZnSe remains.

ZnS windows do not meet 60/40 scratch and dig requirement.

Table 5. Rain Erosion Data--1 Inch/Hour Simulated Rainfall (1.8 mm Diameter Drops)

Specimen ID #		Coating Material (Outside Layer Listed First)	Substrate	Exposure Time at 470 mph (min)	Comments
AFML	Honeywell				
7184	52761	$LaF_3/ZnSe$ (annealed)	ZnS	20	Many small areas of coating removal. Most of coating removed.
7185	52762	$ThF_4/ZnSe$	GaAs	10	About 75 percent of ThF_4 removed after two minutes. A few small isolated spots where ZnSe removed. Substrate cracked.
7186	52763	$LaF_3/ZnSe$	ZnS	20	Coating not removed. Ring cracking in substrate and coating.
7187	52764	$LaF_3/ZnSe$	GaAs	5	LaF_3 completely removed. About 50 percent of ZnSe removed. Substrate cracked.
7188	52765A	$ThF_4/ZnSe$	ZnS	2	About 80 percent of coating removed.
7189	52765B	$ThF_4/ZnSe$ (annealed)	ZnS	20	Ring cracking in substrate and coating. No coating removal except for some very small areas along ring cracks.
7190	52767A	LaF_3 (annealed--air)	ZnS	4	About 25 percent of coating removed. Coating is crazed.
7191	52767B	LaF_3	ZnS	2	Coating completely removed in less than two minutes.
7192	52767C	LaF_3 (annealed--N_2)	ZnS	4	About 75 percent of coating removed. Coating is crazed.

ZnS windows do not meet 60/40 scratch and dig requirement.

Table 6. Rain Erosion Data--1 Inch/Hour Simulated Rainfall (1.8 mm Diameter Drops)

Specimen ID # AFML	Specimen ID # Honeywell	Coating Material (Outside Layer Listed First)	Substrate	Exposure Time at 470 mph (min)	Comments
7437	81276	$NdF_3/ZnSe$	GaAs	5	About 30 percent of coating removed.
7438	81776	$NdF_3/ZnSe$	GaAs	5	About 50 percent of coating removed.
7548	91776	$LaF_3/ZnSe$	ZnS	30	Essentially no coating removal. Several microscopic areas (<0.01") where removal had occurred.
7549	91376	$NdF_3/ZnSe$	ZnS	20	No coating removal even at ring cracks in coating.
7550	91576	$NdF_3/ZnSe$	ZnS	30	Essentially no coating removal except for a few microscopic areas.
7551	72176	$ThF_4/ZnSe$	GaAs	1	About 70 percent of coating removed.
7552	6876	$LaF_3/ZnSe$	ZnS	30	Essentially no coating removed except for a few microscopic areas.
7553	83076	$NdF_3/ZnSe$	ZnS	20	No coating removal.

ZnS windows used meet 60/40 scratch and dig requirement.

3. Based on a comparison of erosion test results of October 12^{th} (Table 6) with those obtained previously, the rain erosion resistance of coatings on ZnS windows with good surface finish exceeding the 60/40 scratch and dig requirement (October 12 data) are superior over coatings on ZnS windows with poor surface finish which do not meet the 60/40 scratch and dig requirement. Figure 23 shows the increased coating damage from rain erosion around two scribe lines in the window surface which were made before coating of the sample was started. The scratch mark in Figure 23 was caused by the edge of the mounting fixture of the erosion tester. The coating damage around the scribe lines is evidence for increased damage rate around imperfections such as scratches, pinholes, etc.

4. The result that the same coatings combinations which survive erosion testing when prepared on good ZnS windows fail when prepared on GaAs windows may be related to the extremely poor surface conditions of the GaAs windows. Repolishing of GaAs substrates was recommended but appeared beyond the scope of the current program.

5. Spectral transmission characteristics of coated ZnS windows measured before and after erosion testing exhibit a degradation of transmission of up to 10 percent due to rain erosion. Representative data is shown in Figure 24 for the NdF_3/ZnSe coatings combination. Microscope pictures taken at Honeywell and AFML show some internal fracturing of ZnS windows after rain erosion which could account for the reduced transmission. Typical internal fracturing is shown in Figure 25 (Honeywell photo).

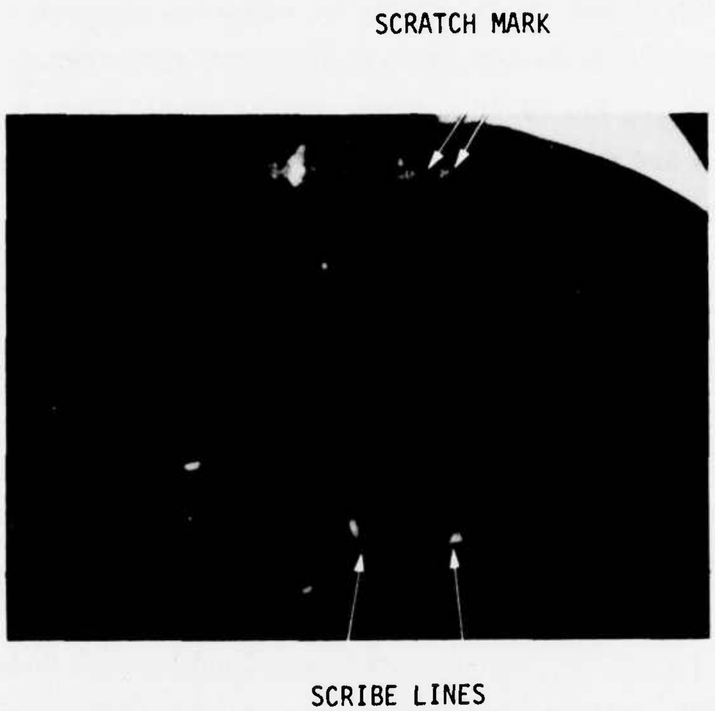


Figure 23. Increased Coating Damage from Rain Erosion Around Two Scribe Lines

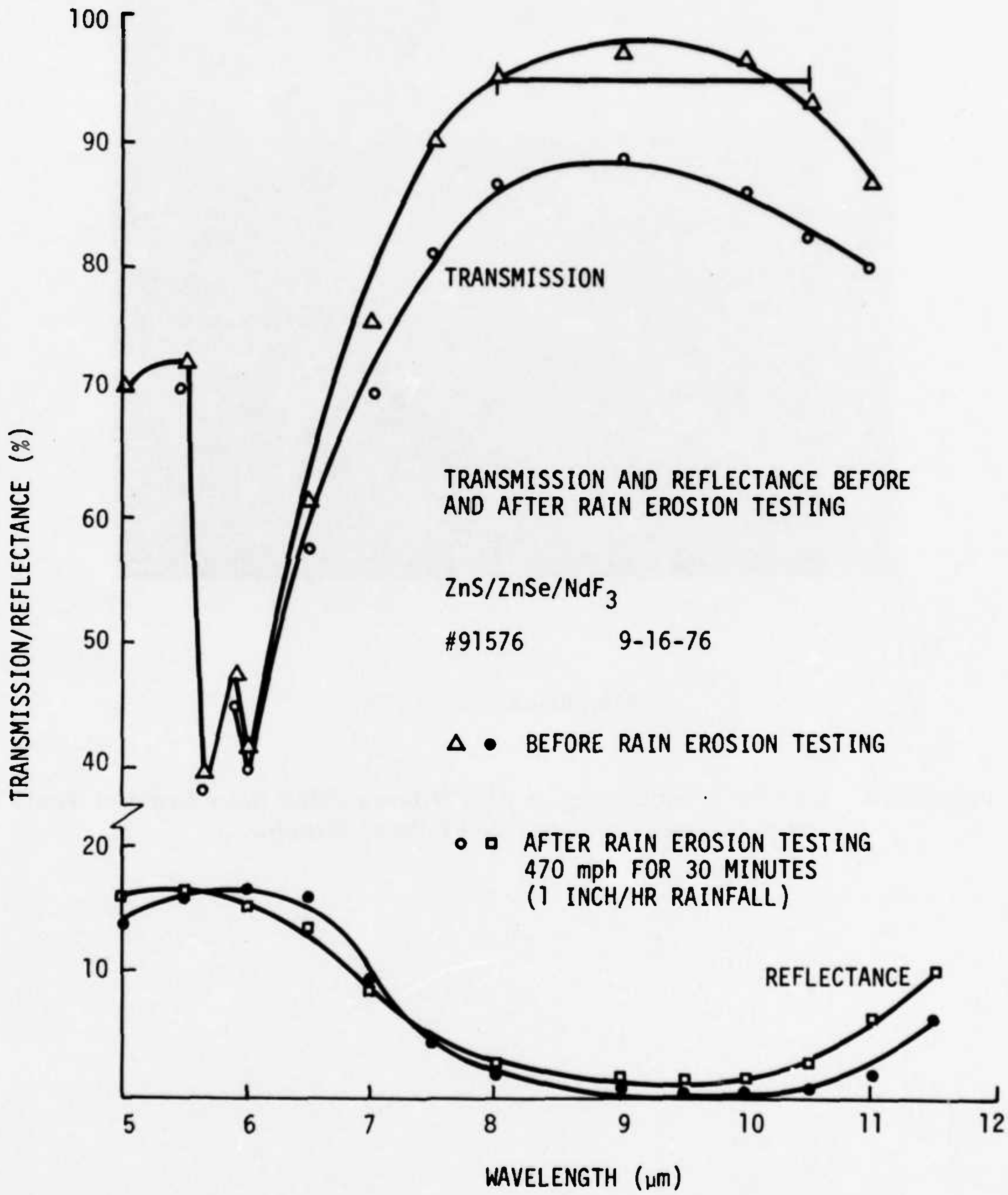
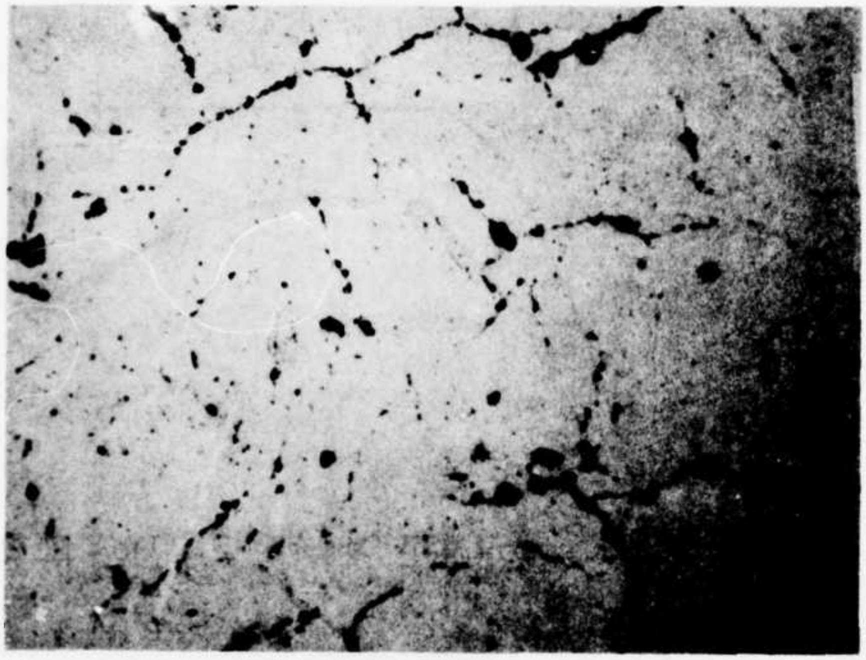


Figure 24. Transmission and Reflectance Before and After Rain Erosion Testing of Coated ZnS Window



Magnification: 100X

Figure 25. Internal Functioning of ZnS Window after Rain Erosion Test. Photo Taken from Uncoated Side of Window.

SECTION XI

VALIDATING MEASUREMENTS

Validating measurements include:

- Transmission measurement at room temperature and 200°C
- Wavefront distortion measurements at 1.06 μm and 10.6 μm modulation transfer function calculations
- Optical homogeniety $\Delta n/\Delta x$ of the AR coatings
- Solubility, humidity, salt spray and abrasion resistance and adhesion properties in accordance with military specifications

Results of validating measurements will be presented in an addendum to this report.

APPENDIX

FABRICATION PROCESS OF EROSION RESISTANT AR COATINGS FOR ZnS IR WINDOWS

HE-158

Honeywell

GOVERNMENT AND AERONAUTICAL PRODUCTS DIVISION CODE IDENT NO. 94580

ENGINEERING SPECIFICATION NO. ES Draft

THIS ENGINEERING SPECIFICATION IS FOR: ☐ SYSTEM ☐ DEVICE ☐ ASSEMBLY ☒ OTHER

LIST DEVICE AND/OR SUBASSEMBLY: Fabrication Process of Erosion Resistant AR Coatings for ZnS IR Windows (Contract No. F33615-76-C-5039)

SIGNATURES	DATE
PREPARED BY J. Brown/W. Doerffler	Nov. 1, 1976
APPROVED BY PROJECT ENGR. H.Y.B. Mar	

REVISIONS

LTR	DESCRIPTION	DATE	APPROVAL	LTR	DESCRIPTION	DATE	APPROVAL

PAGE																											
REVISION																											
PAGE																						PAGE 53					
REVISION																						ES					

Honeywell

GOVERNMENT AND AERONAUTICAL PRODUCTS DIVISION
CODE IDENT NO. 94580

ENGINEERING SPECIFICATION NO. ES Draft

1.0 Materials and Classification

Material	Vendor	Classification and Specification
LaF_3	CERAC/Pure Inc. Milwaukee, WI	1/4" pieces fused, 99.9% (Stock #1-1114) (Lot #4155)
ThF_4	CERAC/Pure Inc.	1/2"-1/8" lumps, 99.9% Anhydrous (Hi-Pur. Optical Gr.), (Stock #TS-106) (Lot #5125)
ZnSe	CERAC/Pure Inc.	1/4" pieces fused, 99.999% optical grade (Stock #Z-1014 (Lot #2297)
NdF_3	Research Chemicals Div., (Nuclear Corp. of America) Phoenix, AZ	1 to 2 μ particle, 99.9%
ZnS windows (polished)	Raw substrates: Raytheon Company Polishing: Advanced Materials Fabrication Optics Comp., Woburn, MA	1.5" x 0.5" x 0.2" Flatness: 1 λ in visible Parallelism: 3 minutes Scratch and dig: 60/40 Edge rounded: 0.08" 6" x 4" x 0.5" Same as above except Parallelism: 20 arc seconds
GaAs window (polished)	Provided by AFML	Required as above

REVISIONS			
LTR	DESCRIPTION	DATE	APPROVAL

2.0 Instrumentation

Honeywell Identification No.			Description of Facility
H-1	650-031		Electron Beam Vacuum Station No. 4 18" Bell Jar 6" Diffusion Pump NRC
H-2			Metal Dessicator with Siligel and Molecular Sieve
H-3	510-5601-001		Sloan-Six/Ten Electron Beam Power Supply and Control
H-4	808-0101-001		Sloan-Y-Axis Beam Control
H-5	808-0202-001		OMNI II--Deposit Thickness Monitor
H-6	350-0609-003		CVC-GIC 300A Ionization Gauge
H-7		● ● ● ● ●	Clean Bench 051-1122 Clean Bench A-2475 Degreaser MPG-695-001 (Trichlorethylene Vapor) Hood Enclosure EL8-5338 EL8-5814 Thermocouple Monitor
H-8	501-951	●	Furnace (Blur M. Electric Co.) Model BFD19
H-9	420-073	●	Flowmeter N_2 (Brooks) Type 5-1110 Full scale = 0.487SCFM
H-10	EL8-5813	●	Flowmeter O_2 (Brooks) Type 2-1110 Full scale = 0.015SCFM

REVISIONS			
LTR	DESCRIPTION	DATE	APPROVAL

2.1 Work Environment

The lab in which the substrates are cleaned and the coatings are fabricated have the following clean room conditions:

Dust/Ft^3:	8K to 50K
Temperature:	65 to 70°F
Relative Humidity:	43 to 52 percent
Static Pressure:	None (positive pressure available)
Filtration:	Electrostatic and Absolute Filters
Clothing:	Smock

3.0 Fabrication and Process Plan

The materials required for the fabrication of erosion resistant AR coatings for IR windows are those described in Section 1.0. All materials are labeled and have been certified.

3.1 Cleaning of Substrates

Note: New substrates are generally contaminated.

REVISIONS			
LTR	DESCRIPTION	DATE	APPROVAL

3.1.1 Soak ZnS substrates for 1 hour in heated (150°F) microdetergent solution, 1000 cm^3 distilled deionized water. Use only clean rubber gloves (surgical) for handlir substrates.

3.1.2 Scrub both surfaces of substrates prepared under 3.1.1 with cotton swabs.

3.1.3 Rinse with warm tap water, then with distilled deionized water.

3.1.4 Immediately follow with blow-dry with dry nitrogen gas directed onto the surface of substrate at an angle such that no water drops from the edges are blown across the surface. Place substrate on lint-free (non-treated) tissue on a "clean bench" or directly into vacuum deposition system.

3.1.5 Vacuum Deposition of Two Layer Coating on ZnS Substrate-- The LaF_3, ThF_4, ZnSe, and NdF_3 vacuum deposition is performed in the bell jar vacuum system (H-1).

3.1.5.1 Place substrates into holding fixture and attach fixture to the substrate heater oven of the vacuum system, using four clips to hold in place. Place thermocouple in hole provided in substrate fixture.

REVISIONS			
LTR	DESCRIPTION	DATE	APPROVAL

3.1.5.2 Install new oscillator crystal for thickness monitor in holder and test thickness monitor for stable oscillation. Adjust for frequency null on monitor. Trim and clean aluminum foil before use in bell jar.

3.1.5.3 Place source materials for first layer coating (ZnSe) and second layer coating (LaF_3 or NdF_3 or ThF_4) into different compartments of the hearth of E-beam unit using a stainless steel scoop. (Pack NdF_3 material thoroughly with a pestle.) The hearths are filled with materials to between 3/4 and 7/8 of their volume.

3.1.5.4 Place clean Pyrex chimney over hearth.

3.1.5.5 Close shutter.

3.1.5.6 Close bell jar and mount protective screen onto vacuum system.

3.1.5.7 <u>Roughing of Bell Jar (Mechanical Pump)</u>

3.1.5.7.1 Check "cold baffle" for being filled with liquid nitrogen (N_2).

3.1.5.7.2 Monitor bell jar pressure (TC-1 gauge).

3.1.5.7.3 Close vent valve.

3.1.5.7.4 Close foreline valve.

3.1.5.7.5 Open roughing valve.

3.1.5.7.6 Continue pumping until pressure is well between 100 μ Hg and 50 μ Hg.

3.1.5.8 <u>Pump Down of System (Diffusion Pump)</u>

3.1.5.8.1 Monitor foreline pressure (TC-2 gauge).

3.1.5.8.2 Close roughing valve.

3.1.5.8.3 Open foreline valve.

3.1.5.8.4 Slowly open gate valve so as not to exceed a foreline pressure of 100 ± 5 μ Hg. Continue until gate valve is fully open.

3.1.5.8.5 Outgas ion gauge (4 ± 1 minutes).

3.1.5.8.6 Adjust zero setting of ionization gauge meter to read zero.

3.1.5.8.7 Adjust emission current to the calibrated value for the gauge. (Value given on calibration tag for the gauge in use.)

REVISIONS			
LTR	DESCRIPTION	DATE	APPROVAL

3.1.5.8.8 Monitor bell jar pressure with ionization gauge.

3.1.5.8.9 After a vacuum of 100 μ Hg has been established, switch on variac for power to the substrate heater oven. Advance variac to reading of 75 $\pm$ 2 percent of full power.

3.1.5.8.10 Allow substrate heater temperature to reach 650° $\pm$ 5°F, then turn variac down to 65 percent of full power. Monitor temperature with thermocouple (H-7).

3.1.5.8.11 Start liquid N_2 flow in Meissner trap, insuring some liquid is always being discharged throughout the deposition cycle.

3.1.5.8.12 Insure shutter is closed.

3.1.5.9 Deposition of Material

3.1.5.9.1 When bell jar pressure is at $3.0 \pm 1.0 \times 10^{-6}$ torr and substrate temperature has stabilized at 650°F for one hour, the system is ready for deposition.

3.1.5.9.2 Bring hearth into position for ZnSe evaporation (first layer).

REVISIONS			
LTR	DESCRIPTION	DATE	APPROVAL

3.1.5.9.3 Sloan Thickness Monitor:

- Set zero adjust on rate meter
- Set range switch to 100 kHz range
- Adjust for frequency null on frequency meter

3.1.5.10 Slowly begin heating material source with electron beam until a smooth rate of 5.0 $\pm$ 0.5 for ZnSe is indicated on thickness monitor with shutter closed. Continue to deposit on shutter until a thickness of 1.0 kHz is indicated.

3.1.5.11 Open shutter and deposit onto substrate until desired thickness plus 1.0 kHz (3.1.5.10) is indicated by Sloan Thickness Monitor.

3.1.5.12 Monitor and record deposition rate pressure and substrate temperature to roughout deposition.

3.1.5.13 Close shutter and turn off electron beam power.

3.1.5.14 Turn hearth into proper position for second layer deposition (LaF_3 or ThF_4 or NdF_3).

REVISIONS			
LTR	DESCRIPTION	DATE	APPROVAL

3.1.5.15 Set zero adjust on rate meter
Set range switch to 100 kHz range
Adjust for frequency null on frequency meter

3.1.5.16 Slowly being heating material source with electron beam until a smooth rate of 5.0 ± 0.5 for LaF_3, or 15.0 ± 1.0 for ThF_4 or 3.6 ± 0.5 for NdF_3 is indicated on thickness monitor with shutter closed. Continue to deposit on shutter until a thickness of 1.0 kHz is indicated.

3.1.5.17 Open shutter and deposit onto substrate with first layer of ZnSe until desired thickness plus 1.0 kHz (3.1.5.15) is indicated by Sloan Thickness Monitor.

3.1.5.18 Monitor and record deposition rate, pressure and substrate temperature 360°F ± 5°F throughout deposition.

3.1.5.19 Close shutter, turn off electron beam power and turn off power to substrate heater.

3.1.5.20 Shut off liquid N_2 to Meissner trap.

3.1.5.21 Wait 45 minutes before warming Meissner trap with compressed air.

REVISIONS			
LTR	DESCRIPTION	DATE	APPROVAL

3.1.5.22 Warm Meissner trap until frost is visible on the external plumbing and bell jar pressure is back in the 10^{-6} torr range.

3.1.5.23 Turn off ionization gauge filament.

3.1.5.24 Monitor foreline pressure (TC-1 gauge).

3.1.5.25 Close gate valve and allow substrate temperature to fall below 100°F (two to three hours).

3.1.5.26 Install blue indicating desiccator to vent valve fitting. (Replace dessicant when pink is indicated.)

3.1.5.27 Open vent valve slowly such that chamber is not exposed to a sudden in-rush of air.

3.1.5.28 When bell jar reaches atmospheric pressure, open chamber and remove fixture and substrate.

3.1.5.29 Remove substrate from holding fixture and inspect for quality and measure reflectance and transmission characteristics.

REVISIONS			
LTR	DESCRIPTION	DATE	APPROVAL

3.1.5.30 Store substrate in desiccated container (H-2) while awaiting the next process step which is the coatings deposition on the second substrate surface.

3.1.5.31 Repeat steps 3.1.5.1 through 3.1.5.29.

3.1.5.32 Store coated substrate in desiccated container (H-2).

4.0 Post Annealing of Coated ZnS Window

4.1 Five hours prior to post-annealing set temperature setting of furnace:

Front 500 Middle 009 Back 500

4.2 Place coated ZnS window into post-annealing fixture and insert into quartz tube outside the post-annealing furnace (H-8).

4.3 Set gas flow:

Nitrogen: Flowmeter (H-9) Setting at 21 $\pm$ 0.5 percent

4.4 Read and adjust furnace temperature to be 200°C $\pm$ 5°C.

4.5 Let gas nitrogen flow take place for 1 hour.

REVISIONS			
LTR	DESCRIPTION	DATE	APPROVAL

4.6 Insert quartz tube into furnace until stainless steel flange touches carbon roller. The duration of heat treatment is 1 hour $\pm$ 5 minutes.

4.7 Monitor and record temperature throughout post-annealing.

4.8 Remove quartz tube from furnace.

4.9 Let quartz tube cool down to room temperature under the continuous flow of N_2.

4.10 Shut off N_2. Open quartz tube and remove window from post-annealing fixture. Store window in desiccator.

5.0 Cleaning of Vacuum System for Coatings Deposition

Remove all aluminum foil from structures inside. Clean system interior, using the wall vacuum hose to remove loose particles. Remove hearth and holding fixture and place it in a solution of 50 percent distilled water and 50 percent concentrated nitric acid for one to two min. Immediately rinse with tap water, then ultrasonically agitate until residues have been removed. Rinse with de-ionized water, then place in over set at 120°F for one hour minimum bake. Mount hearth and holding fixture back into bell jar system. Install new aluminum foil to structures inside system. Outgas holding fixture and hearth for three hours at $3 \pm 2 \times 10^{-6}$ torr.

REVISIONS			
LTR	DESCRIPTION	DATE	APPROVAL

☆ U. S. GOVERNMENT PRINTING OFFICE: 1977 — 757-001/368

DAT

ILM